

THE EFFECTS OF HEAT AND MASS TRANSFER  
ON THE  
SPONTANEOUS HEATING OF COAL

A thesis presented for the  
degree of Doctor of Philosophy in Chemical Engineering  
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by

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1971

*With accompanying material  
in back pocket.*

# ERRATA

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67 9 negligible, the computations were carried out without taking the diffusion of gases in the voids into account.

The results obtained for different rates of flow of the air are shown in figures 30 to 45.

69 8  $\frac{\partial}{\partial t}$  ...

71 2  $C$  ...

76 11  $\delta_{cr} = 0.88$

20 ... if ...

92 13 ... 1957

98 16  $K$  ...

107 13  $\frac{\partial}{\partial t}$  ...

109 7 - ditto -

11 - ditto -

negligible. See figures 28 and 29. Because of these results the computations of unidimensional heat and gas flow (whose results, for different rates of flow of the air, are shown in figures 30 to 45) were carried out without taking the diffusion of gases in the voids into account.

$\varepsilon \frac{\partial}{\partial t}$  ...

$C_i$

$\delta_{cr} = 0.88$  | i.e. if  $\delta > 0.88$  the solid will rise in temperature at an increasing rate. Below  $\delta_{cr}$ , a maximum temperature is reached.

is ...

1957.

126. Bird, R.B., Stewart, W.E., Lightfoot, E.N., "Transport Phenomena", Wiley & Sons, 1960.

$\alpha$  ...

$\varepsilon \frac{\partial}{\partial t}$  ...

- ditto -

- ditto -

THESIS

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## ACKNOWLEDGEMENTS

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### ABSTRACT

Low temperature oxidation of coal was carried out in an insulated container in air currents, the velocities of which had been found to be most favourable in the development of spontaneous heatings. Temperature rises, rate of oxidation and drying were recorded.

A computer program which solves the equations describing the processes considered to be significant in the initial stages of a heating, particularly the moisture transfer, was separately used to obtain the rate of heating and the rate of oxidation of the experiment. The experimental and calculated results were compared, and the calculated results could be made to fit the experimental results by modifying within the range of known practical data the following constants in the oxidation equation:

- (i) temperature dependent coefficient,
- (ii) the order of reaction, and
- (iii) the decrease in the rate of oxidation with the extent of oxidation.

Diffusion, the perfect gas law and vapour pressure - moisture content relationship were included in the processes considered. The results showed that the important processes in spontaneous heatings are the oxidation and the evaporation of moisture of coal.

Conditions under which heaps of coal are likely to fire are determined.

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# NOMENCLATURE

Symbols quoted in Chapter 1 are given in separate lists following this list.

$A$	= temperature at previous time increment	$^{\circ}\text{K}$
$A_o, A_i$	= surface area	$\text{cm}^2$
$C_s, C_p$	= specific heat	$\text{cal/gm } ^{\circ}\text{K}$
$C_I, C_{II}$	= specific heat of coal	$\text{cal/gm } ^{\circ}\text{K}$
$C_2, C_{II}$	= specific heat of the gas phase	$\text{cal/gm } ^{\circ}\text{K}$
$C_a$	= concentration in the gas phase	$\text{gm/cm}^3$
$C_i$	= concentration of component i in the gas phase	$\text{gm/cm}^3$
$d$	= diameter	$\text{cm}$
$D$	= diffusivity	$\text{cm}^2/\text{hr}$
$D_{ij}$	= diffusivity of component i in a binary mixture i-j	$\text{cm}^2/\text{hr}$
$D_{im}$	= effective binary diffusivity of component i in a multicomponent mixture	$\text{cm}^2/\text{hr}$
$D_{ij}$	= diffusivity of the pair i-j in a multicomponent mixture	$\text{cm}^2/\text{hr}$
$E$	= activation energy	$\text{cal/mole}$
$F_1^*$	= dimensionless constant	
$G$	= volumetric rate of flow	$\text{cm}^3/\text{cm}^2 \text{ hr}$
$h$	= heat transfer coefficient	$\text{cal/cm}^2 \text{ hr } ^{\circ}\text{K}$
$H$	= heat transfer coefficient	$\text{cal/cm}^2 \text{ hr } ^{\circ}\text{K}$
(H in Appendix 5 = humidity)		
$j_i$	= diffusional flux	$\text{gm/cm}^2 \text{ hr}$
$k, K, K'$	= thermal conductivity	$\text{cal/cm hr } ^{\circ}\text{K}$
$L$	= latent heat of water	$\text{cal/gm}$
$M$	= dimensionless number	
$M_i, M_j$	= molecular weight	$\text{gm/gm mole}$
$N$	= diffusional flux	$\text{gm/cm}^2 \text{ hr}$



(N on page 98 = dimensionless number)

$O, O_c$	= amount of oxygen consumed	cc of $O_2$ /100 gm of coal
$p$	= partial pressure	atm
$p_o$	= saturation vapour pressure	atm
$q$	= rate of heat generation	cal/cm <sup>3</sup> hr
$Q$	= heat generation	cal/cm <sup>3</sup>
(Q in Table III = amount of oxygen consumed		
		cc of $O_2$ /100 gm of coal)
(Q on page 76	= heat of oxidation	cal/cc of $O_2$ )
$r$	= radial distance	cm
(r on page 76	= distance	cm)
$r_i$	= rate of mass generation of component i in a gaseous mixture	gm/cm <sup>3</sup> hr
$R$	= universal gas constant	cal/gm mole °K
$R_j$	= radial distance	cm
$t$	= time	hr
$T$	= temperature	°K
$T_o$	= temperature	°K
$T_a$	= ambient temperature	°K
$v, v(x)$	= velocity	cm/hr
$V$	= volumetric rate of flow	cm <sup>3</sup> /cm <sup>2</sup> hr
(V on page 97 = volume		cm <sup>3</sup> )
$w_i$	= mass fraction of component i in a gaseous mixture	gm/gm
$W$	= moisture content of coal	gm/gm
$x$	= distance	cm
$X$	= concentration	gm/gm
(X on page 69 = time to travel a distance x		hr)
$y$	= distance	cm
$Y, Y(T)$	= absolute humidity	gm/gm
$z$	= constant	cc of $O_2$ /hr

$\alpha$	= thermal diffusivity	$\text{cm}^2/\text{hr}$
$\delta$	= dimensionless constant	
$\delta_{\text{cr}}$	= critical value of $\delta$	
$\epsilon$	= fraction voids	$\text{cm}^3/\text{cm}^3$
$\lambda$	= thermal conductivity	$\text{cal}/\text{cm hr } ^\circ\text{K}$
$\rho$	= density	$\text{gm}/\text{cm}^3$
$\rho_i$	= density of component i in a gaseous mixture	$\text{gm}/\text{cm}^3$
$\rho_1, \rho_I$	= density of coal	$\text{gm}/\text{cm}^3$
$\rho_2, \rho_{II}$	= density of the gas phase	$\text{gm}/\text{cm}^3$
$\Delta H_{\text{H}_2\text{O}}$	= latent heat of water	$\text{cal}/\text{gm}$
$\Delta H_{\text{O}_2}$	= heat of oxidation	$\text{cal}/\text{gm of O}_2$
$\theta$	= time	hr

#### Subscripts

i	= increment in axial distance
j	= increment in radial distance
k	= iteration step

(k in Appendix 2 = material)

l	= increment in time
---	---------------------

#### SYMBOLS QUOTED IN LITERATURE SURVEY

Symbols used by Scott<sup>79</sup>, pages 7-10

A	= cross-sectional area of the path of flow	$\text{cm}^2$
$C_{\text{pm}}$	= mean specific heat of air	$\text{cal}/\text{mole } ^\circ\text{C}$
f	= size factor, dimensionless	
k	= constant	100 gm of coal/cc of $\text{O}_2$
K	= thermal conductivity	$\text{cal}/\text{gm day } ^\circ\text{C}$

L	= distance from the hot spot to the outside face of the bank	cm
p	= factor for oxygen concentration, dimensionless	
Q	= heat generation	cal/cm <sup>2</sup> cross-sectional area of the path of flow
R	= rate of flow	litres/day cm <sup>2</sup> cross-sectional area of the path of flow
t	= temperature	°C
W	= weight of coal	gm
Ω	= amount of oxygen consumed by coal	cc of O <sub>2</sub> /100 gms of coal
$(\frac{d\Omega}{d\theta})^0$	= initial rate of oxidation of 100 gms of -20+42 mesh coal at an oxygen concentration of 20.93 percent	cc of O <sub>2</sub> /100 gm of coal <sup>2</sup> - day
θ	= time	day
ΔH	= heat of oxidation	cal/cc of O <sub>2</sub>
ΔP <sub>∞</sub>	= pressure difference	cc of water/cm of path of flow

Symbols used by Doornum<sup>23</sup>, pages 11-16

a, a <sub>i</sub>	= temperature coefficient	°C <sup>-1</sup>
A, A <sub>i</sub>	= initial reactivity coefficient	cal/cm <sup>3</sup> hr
b	= temperature coefficient	°C <sup>-1</sup>
B	= initial reactivity coefficient	cal/cm <sup>3</sup> hr
c	= specific heat of coal	cal/gm °C
c <sub>1</sub>	= specific heat of the gas phase	cal/gm °C
F	= surface area	cm <sup>2</sup>
H	= rate of heat dissipation	cal/cm <sup>2</sup> hr °C
K	= thermal conductivity	cal/cm hr °C
L	= rate of heat dissipation	cal/cm <sup>3</sup> hr °C
M, M <sub>i</sub>	= dimensionless number	
N, N <sub>i</sub>	= dimensionless number	
q	= rate of heat generation	cal/cm <sup>3</sup> hr
s	= dimensionless number	

t	= time	hr
T	= reduced time, dimensionless	
v	= temperature	$^{\circ}\text{C}$
V	= volume	$\text{cm}^3$
w	= oxygen concentration expressed in terms of velocity	$\text{cm/hr}$
$\alpha, \alpha_i$	= decay coefficient	$\text{hr}^{-1}$
$\rho$	= density of coal	$\text{gm/cm}^3$
$\rho_1$	= density of the gas phase	$\text{gm/cm}^3$
$\epsilon$	= time constant	$\text{hr}^{-1}$
$\phi$	= reduced temperature, dimensionless	
$\Phi$	= reduced temperature, dimensionless	

Symbols used by Davis and Byrne<sup>19</sup>, page 20

a, b	= constant	hr
K	= constant	$^{\circ}\text{C}$
T	= time	hr
$\theta$	= temperature	$^{\circ}\text{C}$

Symbols used by Schmidt<sup>77</sup>, page 26

b	= constant, dimensionless	
C	= constant	$\% \text{ weight of dry coal}/(\text{day})^b$
R	= rate of oxygen absorption	$\% \text{ weight of dry coal/day}$
t	= time	day
X	= amount of oxygen consumed	$\% \text{ weight of dry coal}$

Symbols used by Yamasaki<sup>124</sup>, page 27

b	= constant	$^{\circ}\text{C}^{-1}$
c	= constant, dimensionless	
T	= temperature	$^{\circ}\text{C}$
X	= amount of oxygen absorbed	$\text{cc/gm of coal}$

Symbols used by Georgiadis and Gailliant<sup>31</sup>, page 28

a	= constant	% wt of coal/hr
k	= constant	hr <sup>-1</sup>
O <sub>2</sub> (bound)	= amount of oxygen absorbed which is unrecoverable as gaseous product	% weight of coal
t	= time	hr

Symbols used by Wood<sup>122,123</sup>, page 29

A	= constant	gm moles/min
B	= constant	gm moles <sup>-1</sup>
t	= time	min
X	= amount of oxygen absorbed	gm moles

## INTRODUCTION

Energy transfer during the spontaneous heating of coal has been expressed by Murtagh and Stott<sup>97</sup> using an energy conservation equation (page xiii) which applies to unidirectional flow of gas through a semi-infinite porous mass (see diagram 1A). Murtagh and Stott solved this equation for boundary conditions similar to those which occur in actual cases of heating and the kinetic data used to describe the oxidation of the coal was derived from results of experiments on sub-bituminous coals similar to those which often fire spontaneously in New Zealand<sup>92</sup>. The equation also introduces a term which describes the drying and wetting of the coal as the hot gases pass through it, and a further term describes the enthalpy changes due to convective heat transfer between the coal and the gas. It was assumed that negligible temperature difference occurred between the mass of gas and the coal and that the air stream was always fully saturated with moisture at the temperature of the point being considered. The solutions of these equations appeared to describe the process of spontaneous heating adequately except at temperatures near the boiling point where it became apparent that the assumed data on oxidation and drying could not provide sufficient heat to evaporate the moisture known to be present. It was therefore desirable to extend Murtagh and Stott's work using more sophisticated assumptions, particularly in regard to drying, to see if the equations could, in fact, duplicate the heating process through and above 100°C.

It was also essential that an experiment be performed in which coal could be made to heat spontaneously under conditions which could be described by the energy equation. Because under practical conditions the direction of gas flow through a coal heap can very rarely be defined with any certainty, the checking of the

energy equation by a laboratory experiment such as described above becomes essential.

It was also considered that the energy equation was deficient in two respects which, although minor, may have had some bearing on the results. These two deficiencies were:

- (1) No correction had been made to the mass of gas in the small elemental volume being considered according to temperature and pressure; that is, in Murtagh and Stott's work the rate of mass flow of gas, i.e. gas density, through the coal heap had been taken to be constant at any point and it is conceivable that Charles' law effects might have a perceptible effect on the results.
- (2) At low rates of gas flow, around 1-2 cm per minute, the effects of diffusion of moisture and oxygen along concentration gradients which exist could also have a real effect on the gas flow. It was therefore desirable to modify the equations to take account of these two effects although this would obviously complicate the solution of the equations considerably.

In the early stages of the work carried out, it was hoped to perform experiments which would produce data on the kinetics of oxidation and drying of the coal which was to be used in the experiments, but as the work proceeded it became apparent that experiments of this nature would have to be severely curtailed if the rest of the aims of the thesis were to be completed in a reasonably short time.

To summarise, the aims of the thesis were:

- (1) to modify the assumptions concerning coal drying used by Murtagh and Stott so that, if possible the equation would describe the spontaneous heating of coal around and beyond 100°C (Chapter 4);

- (2) to perform a laboratory experiment which would produce spontaneous heating in coal under conditions which could be described by the energy equation (Chapter 5);
- (3) to modify the energy equation to include Charles' law correction to the gases as they passed through the coal and to take account of the diffusion of gases along concentration gradients due to oxygen and moisture changes in the gas stream (Chapter 4);
- (4) to produce, if possible, more accurate oxidation and drying data which could be used in the energy equation (Chapter 5).

The first three of these aims were achieved in the thesis but lack of time prevented serious work being carried out on the fourth aim. During the design of the experiment to compare the practical case of spontaneous heating with the energy equation, it was found that a modification in the energy equation would have to be made to describe the experimental design found to be feasible. Although the energy equation quoted above is intended to describe unidirectional flow of mass and heat only, it was found that in any feasible experimental situation flow of heat perpendicular to the flow of gas was appreciable (due to losses from the outside of the container for the coal, see fig.1B) so that modification of the energy equation to take into account this two-dimensional heat flow and later to take into account two-dimensional gas diffusion because of kinetic changes caused by this temperature difference became essential. This modification to the energy equation also caused a marked increase in the computer time necessary to solve the equations. It can be mentioned at this stage that the corrections caused by the introduction of diffusion and Charles' law corrections were found to be negligible under the conditions of spontaneous heating which



were examined in this thesis.

In order to simplify the understanding of the thesis, the major energy equations which were used are now described.

The mathematical simulation of the heating will consist of the following main equations. (The small element of volume under consideration is the small element  $V$  in fig. 1A.)

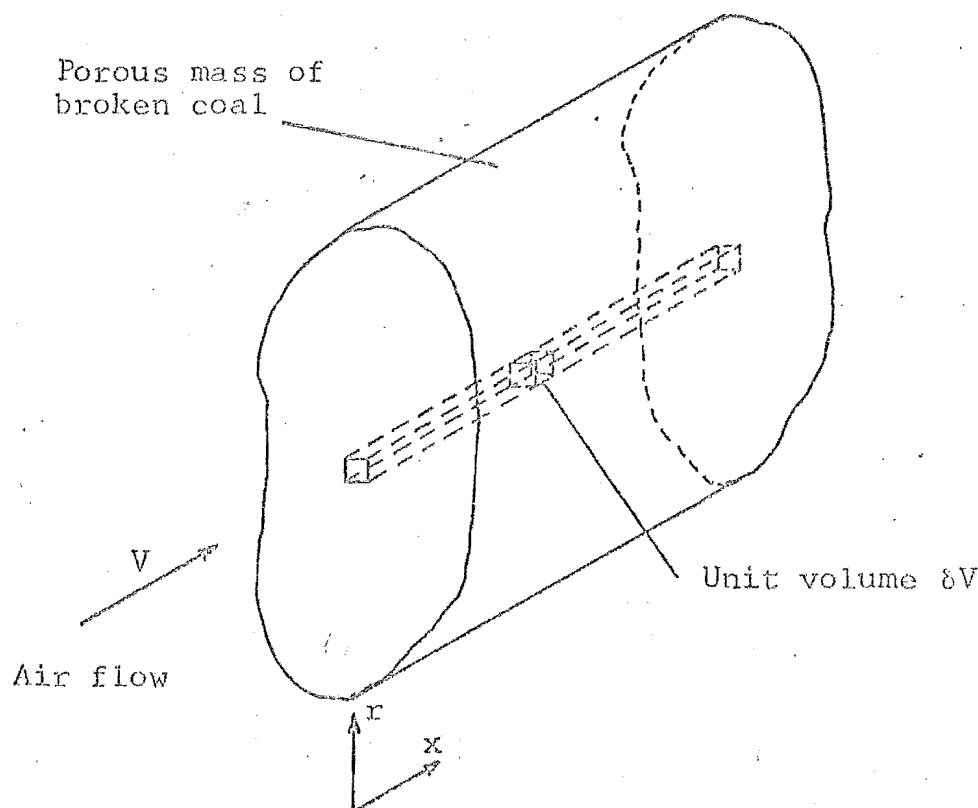


Figure 1A Elementary volume over which energy and mass balance are made

The energy equation is

$$C_I \rho_I \frac{\partial T}{\partial t} = K \nabla^2 T - C_{II} \rho_{II} \vec{V} \cdot \nabla T + \Delta H_{O_2} r_{O_2} - \Delta H_{H_2O} r_{H_2O}$$

Rate of change  
of enthalpy of  
the unit  
volume.

Rate of  
heat trans-  
ferred by  
conduction  
into the  
unit volume.

Rate of heat  
transferred  
to the flow  
because of  
the temp.  
gradient.

Rate of  
heat gen-  
erated by  
the oxid-  
ation at  
unit vol.

Rate of heat  
lost by  
evaporation  
of moisture  
content at  
the unit  
volume.

If the mass of any component of the flowing gaseous mixture changes with time because of the oxidation or evaporation/condensation process, and/or the diffusion process, this has to be described by further equations. This change affects the rate of oxygen absorption  $r_{O_2}$  because the oxygen concentration  $w_{O_2}$  is changed. The rate of evaporation/condensation of moisture  $r_{H_2O}$  and the rate of heat transferred to the flow  $C_{II} \rho_{II} \bar{V} \nabla T$  are also affected by this change because the mass rate of flow  $\rho_{II} \bar{V}$  is changed.

The mass balance equation for a component  $i$  is:

$$\epsilon \frac{\partial}{\partial t} (\rho_i w_i) = - \nabla \cdot (\rho_i w_i \bar{V}) - \nabla \cdot j_i + r_i$$

Rate of mass change of component $i$ in the voids of the unit volume	Rate of mass change of component $i$ in the flow through the voids of the unit volume	Rate of diffusion of component $i$ out of the voids of the unit volume	Rate of mass generated by oxidation or by cond./evap. at the unit volume
--	---	--	--

Mass/unit volume changes with time in the voids of the unit volume and from one unit volume to the next, because of temperature changes with time and distance (Charles' law correction). This produces an equal and opposite percentage change in  $\bar{V}$ . This change in  $\rho_i$  and  $\bar{V}$  affects the terms  $\epsilon \frac{\partial}{\partial t} (\rho_i w_i)$  and  $\nabla \cdot j_i$ .  $r_{H_2O}$  is also changed because two of the terms, which are summed to produce  $r_{H_2O}$ ,  $\nabla \cdot j_{H_2O}$  and  $\epsilon \frac{\partial}{\partial t} (\rho_{H_2O} w_{H_2O})$ , are affected by this change.

The effect of Charles' law becomes appreciable only at low rates of flow and large changes in temperature.

The effect is described by:

$$\frac{\frac{\partial \dot{V}}{\dot{V}}}{\dot{V}} = \frac{\frac{\partial T}{T}}{T}$$

Percentage change in  
volumetric rate of  
flow/unit area

Percentage change in  
absolute temperature

For component i:

$$\frac{\frac{\partial \rho_i}{\rho_i}}{\rho_i} = - \frac{\frac{\partial T}{T}}{T}$$

Percentage change in  
density of component i

Percentage change in  
absolute temperature

These equations take account of changes in  $\dot{V}$  caused by temperature change, and changes in  $\rho_i$ .

To evaluate the diffusional flux described by  $\nabla \cdot \mathbf{j}_i$ , consider the diffusion process<sup>126</sup>. The diffusional flux is the mass flow by diffusion/unit area. The equations which govern the diffusion of a component i in a binary mixture i-j are:

At the steady state:

$$\mathbf{j}_i = -D_{ij} \nabla C_i$$

Diffusional flux

Diffusivity x Concentration gradient

At the unsteady state:

$$\nabla \cdot \mathbf{j}_i = -\nabla \cdot (D_{ij} \nabla C_i)$$

Nett rate of  
accumulation of  
component i at  
unit volume

Change in the diffusional flux/unit distance

The diffusional flux of a component i in a gaseous mixture is given by

$$\mathbf{j}_i = \frac{C_a}{\rho_{II}} \sum_{j=1}^n M_i M_j \mathcal{Q}_{ij} \nabla w_j \quad i = 1, 2, \dots, n$$

where  $\mathcal{Q}_{ij}$  is the diffusivity of the pair i-j in a multicomponent mixture in contrast to  $D_{ij}$  which is the diffusivity of the pair i-j in a binary mixture i-j.

Relations between  $\mathcal{D}_{ij}$  and  $D_{ij}$  can be obtained from the molecular theory of the gases. However, it can also be proved from the molecular theory that for a system where all components move with the same velocity, an effective binary diffusivity, which is given by

$$D_{im} = \frac{1 - w_i}{\sum_{\substack{j=1 \\ j \neq i}}^n \frac{w_j}{D_{ij}}}$$

can be used in the equations which govern the diffusion process in a binary mixture to express the diffusion of component  $i$  in a mixture of  $n$  components.

The effect of the moisture content - vapour pressure equilibrium relationships, the diffusion process and the temperature dependency of the volumetric rate of flow, and the mathematical simulation will be discussed in Chapter 4.

#### Radial Heat Diffusion

In formulating the mathematical model of the experimental simulation of the heating, the heat loss in radial direction of the coal column has to be considered (see Table II, page 56, for details). The mechanism of the heat loss in the radial direction is by conduction through the insulation and by convection at the insulation-air surface. It will be shown that this heat loss is important in comparison with the other processes in Chapter 6 under the heading, "Comparison of low temperature oxidation experiments and calculations", page 53, and in Chapter 7 under the subheading, "Comparison of experimental results and those obtained from computations," page 55.

The mathematical simulation of the experimental oxidation therefore consists of the following set of simultaneous equations.

The mass balance equation is:

$$\epsilon \frac{\partial}{\partial t} (\rho_i w_i) = - \frac{\partial}{\partial x} (\rho_i w_i V)$$

Rate of mass change of component i in the voids of the unit volume

Rate of mass change of component i in the flow per unit volume

$$+ \frac{\partial}{\partial x} (D_{im} \frac{\partial(\rho_i w_i)}{\partial x}) + \frac{\partial}{\partial r} (D_{im} \frac{\partial(\rho_i w_i)}{\partial r}) + D_{im} \frac{1}{r} \frac{\partial(\rho_i w_i)}{\partial r} + r_i$$

Nett rate of diffusion of component i into the voids of the unit vol.

In axial direction

In radial direction

Rate of mass generated by oxidation or by condensation/evap'n at the unit volume

Under the conditions of these experiments, the moisture content of the coal in the experiments will be shown to be only slightly changed from its initial value, so it is not necessary to use the moisture content-vapour pressure relationships, and the air can be assumed to attain saturation humidity. Therefore the saturation humidity is expressed as a function of temperature:

$$Y = a \exp (bT)$$

a, b = constant

Humidity change in the flow per unit time per unit volume is:

$$V_{pII} \frac{\partial Y}{\partial x} = V_{pII} \frac{\partial Y}{\partial T} \frac{\partial T}{\partial x}$$

Amount of water added to the flow per unit time per unit volume

Mass rate of flow per unit area

Change in saturation humidity per unit degree temperature

Temperature gradient in the direction of the flow

The rate of evaporation of moisture of coal in the unit volume is therefore:

$$r_{H_2O} = V \rho_{II} \frac{\partial Y}{\partial T} \frac{\partial T}{\partial x} + \nabla \cdot j_{H_2O} + \epsilon \frac{\partial}{\partial t} (\rho_{H_2O} w_{H_2O})$$

Rate of evaporation to maintain the flow at saturation humidity/unit volume

Rate of diffusion of water vapour out of the voids of the unit volume

Rate of change in absolute humidity in the voids of the unit volume

The rate of oxygen absorption at the unit volume is given by:

$$r_{O_2} = - \frac{a e^{-\frac{E}{RT}}}{(1 + b O_c)^c} (w_{O_2})^d$$

a, b, c: constant.

d: order of reaction with respect to oxygen concentration.

The rate expressions used in the mathematical model are given in Table III.

The energy equations are therefore:

In the coal:

$$C_I \rho_I \frac{\partial T}{\partial t} = K \left\{ \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right\}$$

Rate of enthalpy change of the unit volume

Rate of heat transferred by conduction into the volume

In axial direction

In radial direction

$$- C_{II} \rho_{II} V \frac{\partial T}{\partial x} + f(O_c, T, w_{O_2})$$

Rate of heat transferred into the flow because of the temperature gradient in the direction of flow

Rate of heat generated by oxidation in the unit volume

$$- \Delta H_{H_2O} \left\{ V \rho_{II} \frac{\partial Y}{\partial T} \frac{\partial T}{\partial x} + \nabla \cdot j_{H_2O} + \epsilon \frac{\partial}{\partial t} (\rho_{H_2O} w_{H_2O}) \right\}$$

Rate of heat lost by evaporation in the unit volume.

In the glass and insulation:

$$C \rho \frac{\partial T}{\partial t} = K \left\{ \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right\}$$

Rate of enthalpy change at unit volume	Rate of heat trans- ferred by conduction into the unit volume	In axial direc- tion	In radial direction
--	--	-------------------------------	------------------------

At the interfaces of the materials:

$$K \left( \frac{\partial T}{\partial r} \right)_{\text{interface}} = K' \left( \frac{\partial T}{\partial r} \right)'_{\text{interface}}$$

Rate of heat leaving one material in the radial direction/unit area	Rate of heat entering the other material in the radial direction/unit area
---	--

At the air-insulation interface:

$$K \left( \frac{\partial T}{\partial r} \right) = h (T - T_a)$$

Rate of heat leaving the insulation/unit area	Rate of heat loss to the air/unit area
---	---

Change in mass per unit volume and the volumetric rate of flow due to Charles' law is as described by the equations given on page xv.

The method of solution of the set of equations is discussed in Chapter 6 under the heading: "Method of computation". Details of the method of solution are given in Appendices 2 and 3.

## Moisture Content-Vapour Pressure Relationships

When change of relative humidity with moisture content has to be taken into account, that is as the temperature approaches 100°C and drying becomes appreciable, the terms which describe the vapour pressure of water in the gas phase are modified. The set of equations which simulate a heating caused by a unidirectional flow of gas under these conditions is as follows:

The mass balance equation is:

$$c \frac{\partial}{\partial t} (\rho_i w_i) = - \frac{\partial}{\partial x} (\rho_i w_i V) + \frac{\partial}{\partial x} (D_{im} \frac{\partial (\rho_i w_i)}{\partial x})$$

Rate of mass change  
of component i in  
the voids of the  
unit volume

Rate of mass  
change of  
component i in  
the flow per  
unit volume

Rate of diffusion of  
component i into the  
voids of the unit  
volume

+  $r_i$

Rate of mass generated by oxidation  
or by condensation/evaporation at  
the unit volume

The rate of oxygen absorption  $r_{O_2}$  at the unit volume is as described on page xviii.

The equilibrium humidity of the air is expressed as functions of temperature and moisture content of the coal:

$$Y = g(W) k(T)$$

The functions are given in Table III, and in Appendix 4, page 110.

Humidity change in the flow per unit time per unit volume is:



$$V_{p_{II}} \frac{\partial Y}{\partial x} = V_{p_{II}} \left\{ k(T) \frac{\partial Y}{\partial W} \frac{\partial W}{\partial x} + g(W) \frac{\partial Y}{\partial T} \frac{\partial T}{\partial x} \right\}$$

Amount of water added to the flow per unit time per unit volume	Mass rate of flow per unit area	Change in equilibrium humidity due to temperature and moisture content gradient in the direction of the flow
--	--	---

The rate of evaporation of moisture of coal at the unit volume is therefore:

$$r_{H_2O} = V_{p_{II}} \frac{\partial Y}{\partial x} + \frac{\partial}{\partial x} (j_{H_2O}) + \epsilon \frac{\partial}{\partial t} (\rho_{H_2O} w_{H_2O})$$

Rate of evap- oration to maintain the equilibrium humidity of the flow/ unit volume	Rate of diffusion of water vapour out of the voids of the unit volume	Rate of change in absolute humidity in the voids of the unit volume
---	--	--

The energy equation is therefore:

$$C_{IpI} \frac{\partial T}{\partial t} = K \frac{\partial^2 T}{\partial x^2} - C_{II} p_{II} V \frac{\partial T}{\partial x}$$

Rate of enthalpy change of the unit volume	Rate of heat transferred by conduction into the unit volume	Rate of heat transferred into the flow because of the temperature gradient in the direction of flow
--	--	--

$$+ f(0_c, T, w_{O_2})$$

Rate of heat generated by  
oxidation at the unit volume

$$-\Delta H_{H_2O} \left\{ V_{p_{II}} \left\{ k(T) \frac{\partial Y}{\partial W} \frac{\partial W}{\partial x} + g(W) \frac{\partial Y}{\partial T} \frac{\partial T}{\partial x} \right\} + \frac{\partial}{\partial x} (j_{H_2O}) + \epsilon \frac{\partial}{\partial t} (\rho_{H_2O} w_{H_2O}) \right\}$$

Rate of heat lost by evaporation at the unit volume

Change in mass/unit volume and the volumetric rate of flow due to Charles' law can again be described by the same equations discussed on page xv.

The method of solution of the set of equations is described in Appendix 4. Discussion of the solutions of the set of equations is given in Chapter 7, under the heading:

"The significance of results from the simulation", page 65.

The above set of equations comprises the main ones used in the thesis.

The following terms which denote the state of moisture held in coal and have been used by previous investigators under different names are defined here.

Bound moisture<sup>64</sup> = The difference between the moisture which can be removed at 250°C and the moisture which can be removed at a specified temperature by prolonged drying in an inert atmosphere.

Equilibrium moisture content = Moisture content which is at equilibrium with the vapour pressure of water in the air.

Capillary water or combined water = Moisture content of coal (as determined by British Standard Specification Proximate Analysis).

Inherent water, natural moisture content, initial moisture content = Moisture content of freshly mined coal.

Intrinsic water<sup>65</sup> = Water produced by the oxidation of coal.

## CHAPTER ONE

### INTRODUCTION AND LITERATURE SURVEY

#### 1. SPONTANEOUS HEATING

It has long been known that coal piles can develop self-heating. A full understanding of spontaneous heating is desirable in order to prevent its occurrence. The waste of mineable coal and the danger caused by mine fires and the weathering of coal by heating and slow oxidation in storage piles, cause an appreciable loss and hence heavily affect the economics of coal mining. It is estimated that in bord and pillar working fifty per cent of otherwise mineable coal can be lost because of mine fires<sup>92</sup>.

It is now generally accepted that the oxidation of coal is the main cause of spontaneous heating. The generation and dissipation of heat in a coal pile which determine whether the pile would develop a heating, depend on the heat transport processes, the oxidation of coal and the moisture transfer.

Before the middle of the last century it was thought that iron pyrites was the cause of the spontaneous combustion. In the middle of the last century, the first methodical experiments carried out in the laboratory on the spontaneous heating of coal were begun. Coal in lump and fine forms were shown to gain oxygen and liberate carbon dioxide at room temperature and upwards. By 1866, it had been shown that the absorption of oxygen, which was accompanied by an evolution of heat, could account for spontaneous heating.

Richters<sup>16</sup> made the first systematic examination of the subject. In a series of experiments the products of the oxidation, carbon dioxide and water, and the amount of oxygen fixed by the coal were measured.

By the end of the nineteenth century, the capacity of coal to react with oxygen at an increasing rate at increased temperatures, had been established. Spontaneous combustion was thought to occur when the coal presented a sufficient surface to the air and was sufficiently insulated thermally.

#### Oxidation of pyrites

Iron pyrites exists in coal in two crystalline forms, the cubic (yellow pyrites) and the rhombic (marcasite).

The oxidation of pyrites in moist air gives sulphuric acid and hydrate ferrous sulphate. The sulphuric acid may become neutralised by carbonates of calcium, magnesium and iron, often present in the coal strata. The heat of reaction is 316 Kcal, which is equivalent to 4 cal/cc of oxygen. Marcasite produces 321.6 Kcal/mole. The products have a greater volume than the original pyrites and hence break the coal in which they are embedded and so expose a greater surface of coal to the air.

The characteristics of pyrites oxidation are that the rate is higher than that of carbonaceous matter at the same temperature, and does not fall off with time as rapidly. The size of the particles has a more marked effect with pyrites than with coal, the products can be washed away and the absorption rate can then regain some of its initial value. These factors have led many investigators to suggest that the

oxidation of pyrites is the main cause of spontaneous heatings.

Winmill<sup>109</sup> measured the rate of production of heat by the oxidation of pyrites at mine temperatures.

Graham<sup>42</sup> extended Winmill's experiments and found that a considerable proportion of the oxidation of the coal samples was often due to the pyrites. However, it was concluded that pyrites can only be the cause of a heating if the pyrites were present in high proportion and in a finely divided state.

Parr et al<sup>16</sup> suggested that the pyrites were important in the second stage of the oxidation. It was shown that the oxidation of one-fifth of the quantity of pyrites present in the average Illinois coal would be capable of raising the temperature of an insulated mass of coal to near the temperature for autogeneous oxidation.

Mapstone<sup>68,69</sup> has suggested that organic peroxide may oxidise pyrites to ferrous sulphide which is pyrophoric.

McPherson, Simpkin and Wilet<sup>77</sup> reached the conclusion that although pyrites may assist in a minor degree in the self-heating of coal, their most important effect is the disintegration caused to the coal by its oxidation.

Davis<sup>125</sup> has pointed out that conceivably pyrites may heat more rapidly than the coal substance at a critical point and thus accelerate the heating disproportionally. However, inflection points in oxidation curves have not been found, therefore it seems doubtful if the pyrites can exert the effect supposed.

It is generally accepted that the contribution of the

oxidation of pyrites was small in comparison with the heat arising from the slow oxidation of the coal itself.

#### Heating due to bacteria

Potter<sup>16</sup> measured the rate of liberation of carbon dioxide and the thermal effects of inoculated and sterilized samples. It was found that the inoculated coal produced carbon dioxide and a small temperature rise.

It has been suggested that bacterial action might contribute to the spontaneous heating of coal.

Various types of bacteria can oxidise methane and other coal substances. However, the effect of micro-organisms generally has a minor influence<sup>16</sup>.

#### Heating due to friction

The crushing of coal under the pressure of superincumbent strata has been suggested as a source of heating contributing to spontaneous combustion. It was found that crushing is important because it increases the surface of coal<sup>16</sup>.

#### Heating due to extraneous matters

Oxidation of the coal surrounding timber may raise the temperature to the ignition temperature of wood, which is lower than coal<sup>16</sup>, and hence cause the heating of the coal. Other inflammable matters such as oil, lubricants, can be found in mines, but practical experience does not suggest that unaided they can cause self-heating.

#### Oxidation of coal and spontaneous heating

The oxidation of coal has been studied extensively. One of the most extensive and systematic researches on coal oxidation was carried out by Winnill and Graham. Their

experiments covered all aspects of the oxidation of coal that are useful for the investigation of spontaneous heating.

Winmill<sup>106</sup> explained the development of heatings in a coal pile by the balance between the rate of heat loss and the rate of heat production. It was pointed out that initial temperature could play a critical part.

Haldane<sup>54</sup> gave a description of the processes which eventually lead to heating. He stated that owing to the mine ventilation, a continuous slow current of air passes horizontally through a layer of coal. The heat produced by oxidation in each layer of the coal is carried onwards to the next layer and the temperature rises higher and higher along the course of the air current, until at a certain distance a dangerous temperature is reached. The heat carried forward by the air current includes the latent heat due to evaporation of moisture. The latent heat, deposited further on becomes more and more important as the temperature approaches boiling point. The moisture in coal must be evaporated before the temperature can rise above boiling point and the large amount of heat required retarded the heating of coal. The coal which has been considerably raised in temperature by deposition of moisture will combine with a far greater amount of oxygen than at a lower temperature.

However, the effects of the physical conditions on calculations of the liability of spontaneous heating was considered only much later. The physical factors which should be investigated were listed by one investigator<sup>101</sup> as follows:

The characteristics of the air current which are affected by:

- the volume and movement of the ambient air;
- the underpressure or degree of vacuum created by fans;
- the physical properties of the intake air such as humidity, barometric pressure;
- the system and method of ventilation;
- the resistance of the airways;
- the gas contents of the seam and the mechanism of gas liberation;
- the seasonal change in atmospheric pressure;
- the pressure gradient along the passage of the air flow.

The investigation of the surroundings of the zone of heating should extend to:

- the geological conditions and characteristics of the rocks;
- the system and method of mining;
- the dimension of the coal measures and the coal seam;
- the inclination of the seam;
- the degree of fragmentation of the seam;
- the main characteristics of the faults and folded zones;
- the strength properties of the roof layers and super-incumbent strata;
- the moisture content of the strata and its replenishment;
- the range and intensity of the rock movement in space and time;
- the thermal conductivity of the surround materials.

The list shows that the number of factors which can affect the physical conditions of spontaneous heating, is numerous.



Scott<sup>79</sup> obtained data on the oxidation of anthracite from experiments and gave an evaluation of the liability to heatings. This was one of the first methods proposed, with numerical examples. The process which generated heat was the oxidation of coal. The oxidation depends on: temperature, partial pressure of oxygen, particle size of coal, degree of oxidation of coal, composition of coal and humidity of the circulating air. The dissipation of heat was produced by losses due to circulating gases, conduction, radiation and convection. The rate of circulation depends on the driving potentials and resistance. The driving potentials are the sum of pressure differences due to temperature difference (chimney effect), wind velocity, barometric changes, change in volumes due to chemical reaction and diffusion. The resistance due to circulation depends upon temperature, particle size, particle shape, voidage, circulation rate, condensed and capillary water. Scott also took into account the extra heat needed to evaporate rain water falling on coal heaps. Losses by conduction, radiation and convection depend upon: temperature gradient, thermal conductivity of coal, temperature differences between surface of bank and surroundings, area of surface and wind velocity.

A rate of heat generation in a pile of anthracite was obtained from the kinetics experiments on oxidation, as follows:

$$\frac{dG}{d\theta} = \Delta H \cdot p \cdot f \cdot \frac{W}{100} \left( \frac{d\Omega}{d\theta} \right)^0 e^{-k\Omega}$$

where  $\Delta H$  = heat of oxidation/cc of oxygen consumed

$p$  = factor for oxygen concentration

$$= \frac{20.93 - [O_2]}{20.93 \ln \frac{20.93}{[O_2]}}$$

$W$  = weight of coal in gms

The pressure difference caused by the defficiency of the oxygen was

$$\Delta p_{\infty} = \frac{300}{888} \times \frac{1.309}{1000} \times 0.83 \frac{(20.93 - [O_2])}{100}$$

cm of water / cm of path

The flow due to this pressure change was:

$$R = 4.86 \times 10^4 (20.93 - [O_2])^{0.517} \text{cc/day}$$

The initial oxidation rate was:

$$\begin{aligned} \left(\frac{d\Omega}{d\theta}\right) &= p f \frac{W}{100} \left(\frac{d\Omega}{d\theta}\right)^0 \\ &= R \frac{(20.93 - [O_2])}{100} \end{aligned}$$

Therefore  $[O_2] = 20.31$  percent

$R = 42.7$  liters per day per square centimeter.

Scott stated that this has little significance under ordinary conditions, but this seems doubtful. The change in circulation rate due to diffusion of air was negligible. The flow due to changes in barometric pressure was found to be 11.5 cc of air per square centimeter entering and leaving the bank per day.

Applying the Torricelli's law, flow resulted from a wind of 10 miles per hour blowing horizontally against the 300-foot bank at 25°C was 45.75 liters per day per sq.cm.

A temperature curve was fitted with a parabolic equation and differentiated. The following equation was obtained:

$$\frac{dt}{dL} = \frac{0.881 (\Delta t)}{L^{2.53}}$$

where  $\Delta t$  was the temperature difference between the hot spot and the outside surroundings of the bank, and  $L$  was the the distance from the hot spot to the outside surface of the bank.

The rate of heat flow was:

$$\frac{dQ}{d\theta} = kA \frac{0.881 (\Delta t)}{L^{2.53}}$$

$$= mkA (\Delta t)$$

This slow dissipation of heat showed that a mass of coal in full combustion might require a long time to cool and that the admission of air would restart the fire if not sufficiently cooled.

The 300 ft bank of coal was considered. The longest path of travel was 888 feet, and the weight of coal along this path would be 23,100 grams/cm<sup>2</sup>. The size of the coal was assumed to be between  $\frac{11}{16}$ " and  $\frac{9}{10}$ ". The rate of oxidation along the path was

$$\left(\frac{dQ}{d\theta}\right)_G = \Delta H \cdot p \cdot f \cdot \frac{W}{100} \left(\frac{d\Omega}{d\theta}\right)^0 e^{-k\Omega}$$

$$= 4.7 \times 1 \times 0.0556 \times \frac{23100}{100} \left(\frac{d\Omega}{d\theta}\right)^0 e^{-k\Omega}$$

$$= 60.3 \left(\frac{d\Omega}{d\theta}\right)^0 e^{-k\Omega}$$

where  $\left(\frac{d\Omega}{d\theta}\right)^0$  was the initial oxidation rate of the 20 to 42 mesh size.

The average atmospheric temperature was 25°C, coal was assumed to be dry and air 50 percent saturate at 25°C, and no rain. Complete absence of winds and negligible conduction losses were assumed.

Therefore the heat losses due to the circulating air was:

$$\left(\frac{dQ}{d\theta}\right)_L = \frac{R}{22.4} \times C_{pm} \times \Delta t$$

The calculation was carried out as follows:

As the temperature was 25°C, the "integrated average" or effective oxidation temperature was also 25°C. The rate of heat generation was therefore 4,000 calories per day, initially the actual rate was also 4,000 calories per day as  $\Omega = 0$ .

The heat loss was  $\left(\frac{dQ}{d\theta}\right)_L = 0$  as  $\Delta t = 0$ . The rate of temperature rise was therefore 0.734°C/day. At this rate the time required to reach 35°C was 13.62 days. The oxygen consumed during this period was found by:

$$\begin{aligned}\frac{d\Omega}{d\theta} &= f \left(\frac{d\Omega}{d\theta}\right)^0 e^{-k\Omega} \\ \int e^{k\Omega} d\Omega &= \int f \left(\frac{d\Omega}{d\theta}\right)^0 d\theta \\ e^{k\Omega} - e^{k\Omega_i} &= kf \left(\frac{d\Omega}{d\theta}\right)^0 \theta\end{aligned}$$

$k$  and  $f\left(\frac{d\Omega}{d\theta}\right)^0$  were evaluated from temperature 31°C, hence the value of  $\Omega$  was obtained. The mean path temperature was now at 35°C. The effective oxidation temperature was 36°C. The rate of heat generation and rate of heat losses at these conditions were evaluated. Therefore a new rate of temperature rise was obtained. The cycle of calculations was repeated until this value became negative or increased at an accelerated rate.

Van Doormum<sup>23</sup> gave a procedure for the calculation of the temperature rise in a reacting coal pile, in which the reactivity of the coal was obtained from experiments with an adiabatic calorimeter. The dissipation terms depended on the shape and dimension of the coal pile, size grading and the ventilation. The calorimeter was constructed so that the conditions were nearly isothermal, and therefore the

rate of oxidation at different temperatures could be measured. The relationship

$$q = f(v, t, w)$$

where  $q$  = heat generation

$v$  = temperature

$t$  = time

$w$  = oxygen concentration expressed in terms of oxygen space velocity

could be determined. The rate of heat generation was expressed by the following equation:

$$q = \sum_i A_i \exp(a_i v - \alpha_i t)$$

where  $A_i$  was an initial reactivity coefficient,  $a_i$  was a temperature coefficient, and  $\alpha_i$  was a decay coefficient. The dependency of the absorption on the rate of supply of oxygen was found to follow the following equation:

$$p = p_m \frac{w}{w + w_m}$$

$p_m$  was the maximum absorption rate,  $w_m$  was a characteristic constant.

The temperature rise was given by the equation

$$\rho c \frac{\partial u}{\partial t} = K \Delta^2 v - \nabla \cdot (\bar{W} \cdot v) + q$$

where  $\rho$ ,  $c$  were the density and specific heat respectively of coal

$K$  thermal conductivity

$$\bar{W} = \bar{w} \rho_1 c_1$$

$\rho_1$ ,  $c_1$  were the density and specific heat respectively of air or oxygen.

Initially, the temperature of the coal was zero, and the temperature of the exposed surface was zero.

Approximations involving the shape of the pile were introduced. The coal pile was assumed to be homogeneous, and in the following treatment the oxygen supply was in excess.

The method to solve the above equation was built up in three steps:

- (i) Taking only the decay effect into account.
- (ii) Considering the temperature effect only.
- (iii) Accounting for both effects simultaneously

Heat generation as a function of the time only.

In this case:

$$q = \sum_i A e^{-\alpha_i t}$$

or  $q = A e^{-\alpha_i t}$

This simplification could be applied only in cases where the temperature rise was small.

For an insulated container:

$$V \rho c \frac{dv}{dt} = V A e^{-\alpha t} - FHv$$

where  $V$  = volume

$F$  = exposed surface

$H$  = heat dissipation per degree of temperature rise per unit time per unit surface area,

or  $\frac{dv}{dt} = \frac{A}{\rho c} e^{-\alpha t} - \epsilon v$

where  $\epsilon = \frac{FH}{V\rho c}$

Van Doormum claimed that the total quantity of heat released  $Q$  under isothermal conditions has been found to be not appreciably affected by the rate of release. Therefore:

$$\begin{aligned} Q &= \int_0^{\infty} q dt = \text{constant} \\ &= \int_0^{\infty} A e^{-\alpha t} dt \end{aligned}$$

It followed that the maximum temperature rise attainable was:

$$v_m = \frac{A}{\alpha \rho c}$$

If  $\phi = \frac{v}{v_m}$

$$T = \epsilon t$$

$$N = \frac{\alpha}{\epsilon}$$

$$\frac{d\phi}{dt} = N e^{-NT} - \phi$$

The solution to this equation was:

$$\phi = \frac{N}{1-N} (e^{-NT} - e^{-T})$$

when  $N \neq 1$

$$\phi = T e^{-T}$$

when  $N = 1$

These equations expressed the transient temperature rise as the result of the heat released by oxidation in quasi-isothermal conditions. For example, a coal stack of height  $h = 200$  cm was piled on an insulating base, for this coal  $A = 0.005$ ,  $\alpha = 0.001$  and  $\rho c = 0.25$ ,  $v_m$  was  $20^\circ\text{C}$  and  $N$  was 4 for  $k = 4 \text{ cm}^2/\text{hr}$ . The maximum temperature rise was found to be  $15^\circ\text{C}$  after 2,040 hours.

#### Decay effect neglected

The heat generation was approximated by:

$$q = Be^{bv}$$

for the insulated container, the temperature rise follows the equation:

$$\rho c \frac{dv}{dt} = Be^{bv} - Lv$$

$$\text{If } \Phi = bv$$

$$T = \epsilon t$$

$$\epsilon = \frac{L}{\rho c}$$

$$S = \frac{Bb}{L}$$

$$\text{then } \frac{d\Phi}{dt} = Se^{\Phi} - \Phi$$

which may be integrated numerically. The criterion for a stable state was therefore

$$S \leq e^{-1} = 0.368$$

which gave the maximum temperature  $\Phi = 1$ . However, unless the value of  $S$  was grossly exceeded, a dangerous temperature rise might not occur during the lifetime of a pile. For example, when  $S = 0.5$ , the temperature  $\Phi = 1$ , corresponding to a temperature rise of the order  $25^{\circ}$  to  $40^{\circ}\text{C}$ , would be attained after 11,200 hours.

It could be seen that  $S$  depends on the initial temperature and the decay factor. When a reaction of considerable length was involved, the decay factor would appreciably affect the issue. Therefore it had to be included.

#### Heat generation a function of both temperature and time

Considering a single term:

$$q = Ae^{av-qt}$$

In the adiabatic case



$$\rho c \frac{dv}{dt} = Ae^{\alpha v} - \alpha t$$

$$\text{If } \Phi = av$$

$$T = \alpha t$$

$$M = \frac{Aa}{\alpha \rho c}$$

$$\text{then } \frac{d\Phi}{dT} = Me^{\Phi - T}$$

The solution was:

$$\Phi = -\ln(Me^{-T} + 1 - M)$$

When  $M \leq 1 - e^{-1} = 0.632$ , the temperature rise  $\Phi = 1$  was not exceeded.  $M$ , like  $S$ , was a function of the temperature.

For the insulated container, the temperature rise followed the equation:

$$\rho c \frac{dv}{dt} = Ae^{\alpha v} - \alpha t - Lv$$

$$\text{or } \frac{d\Phi}{dT} = Me^{\Phi - T} - \frac{\Phi}{N}$$

The solutions were obtained by numerical integration. When more than one component had to be taken into account, several parameters

$$M_i = \frac{A_i a_i}{\alpha_i \rho c} \quad \text{and} \quad N_i = \frac{\alpha_i}{\epsilon}$$

had to be considered.

The criterion obtained was  $\sum M_i \leq 0.632$  where the smallest  $\alpha_i$  which expressed the long persistence of the oxidation had the highest  $M_i$  value.

From the results obtained, the following conclusions were reached:

- (i)  $M < 0.632$  : the coal could be safely stored under any conditions when the initial temperature did not exceed a certain value.

- (ii)  $N(M-1) \geq 1$ : spontaneous heating would occur.
- (iii)  $N(M-1) < 1$ : safe storage depended on values of  $N$  and  $M$ .

The parameters  $M_i$  for a coal were mainly dependent on its initial temperature and size grading and were not much affected by ventilation. The parameters  $N_i$  might be affected by the ventilation, as increased ventilation supplied more oxygen, and therefore had an effect on  $\alpha_i$ , while for  $M_i$  both  $A_i$  and  $\alpha_i$  varied in the same direction.

When the ventilation was not sufficient to provide the coal pile with all the oxygen it could absorb; heat generation could be found to be reduced to a surface layer to which an effective depth  $y$  and a parameter  $N_i = gy^2$  might be used.

Therefore it could be seen that when the condition  $\sum_i M_i < 0.632$  was not satisfied, the conditions which decided whether spontaneous combustion would occur depended on external conditions such as the size and the shape of the coal pile and its ventilation.

The parameter  $M_i$  could be determined from laboratory tests. However, calculations on a bunker test, with subsequent laboratory tests, failed to prove this fact.

### Reactivity of Coal

The reactivity of coal is a measure of the tendency of coal to react with oxygen and is therefore related to spontaneous heatings. The measurement of reactivity is carried out by different methods.

#### 1. Oxygen absorption

Measurements of oxygen absorption make a considerable

contribution to the study of the oxidation of coal, and, with the inherent moisture content, give the most reliable comparisons of the tendencies of various coals to spontaneous combustion.

Heat production can be measured by an isothermal calorimeter<sup>61,92</sup>.

If the oxygen absorption is measured at the same time, the heat of oxidation per unit mass of oxygen absorbed can be obtained. The quantity of oxygen absorbed is obtained either by gas analysis from constant pressure, flow experiments, or from the pressure change in a constant volume system<sup>84</sup>.

## 2. Absorption of Halogens

It was found that coal exposed to air for a few hours at 130°C absorbed much less bromine than the unexposed coals. This fact suggested that the halogen absorption can be used to measure the tendency to spontaneous combustion<sup>12</sup>.

## 3. Relative ignition temperature

The ignition temperature has been used as a measure of the reactivity of coal. Ignition temperature is the temperature at which the reactant begins to rise in temperature above the surrounding temperature when heated at a steady rate of rise of temperature.

Davis and Byrne<sup>16</sup> showed that there was a regular decrease in ignition temperature as the particle size was reduced from 10 - 20 mesh to below 200 mesh. Scott<sup>79</sup> measured the ignition temperature of different types of coal. The ignition temperature of anthracites varied between 416°C and 528°C, the values for bituminous and subbituminous coals

ranged from 186°C to 420°C.

Schroeder<sup>125</sup> found that ignition temperatures increased linearly as volatile matter decreased to about 15-18 percent, but rose much more rapidly as the volatile matter decreased further. Fresh coal samples had lower ignition temperature than oxidised coals.

Mixtures of coal with an oxidising agent have been used to measure the ignition temperature.

#### 4. Differential thermal analysis

The temperature difference between a reacting mass and an inert mass are measured as the temperature is raised steadily.

Stott and Baker<sup>85</sup> found that the endothermic trough on the differential thermal analysis curves obtained for the lower rank coals corresponded to the amount of heat necessary to evaporate the moisture content.

#### 5. Direct observation

Experimental heatings have been carried out to measure the temperatures developed and the gases evolved. However the surrounding conditions cannot be closely controlled and it has not been possible to correlate the results with the variables.

#### 6. Adiabatic experiments

Adiabatic tests are the most direct method to measure the tendency of a coal to heat spontaneously.

Since in practice there is practically no heat exchange between the coal and its surrounding as coal and

rock are poor conductors of heat, adiabatic experiments closely parallel the rate of oxidation and the gaseous products obtained as the coal undergoes changes in temperatures with those obtained in practice.

Winmill<sup>106</sup> used a vacuum flask whose temperature was controlled to be  $0.2^{\circ}\text{C}$  higher than a surrounding water bath. A regulator kept the temperature of the bath varying similarly to the temperature in the reaction flask and thus ensured that the heat lost was negligible.

Dried coals were found to fire after 24 hours in a current of oxygen. In a current of air they rose to  $150^{\circ}\text{C}$  after 30 hours. Coals containing their natural moisture content were found to rise from  $19^{\circ}\text{C}$  to  $110^{\circ}\text{C}$  after 40 hours. The rate of heating above  $50^{\circ}\text{C}$  was much slower because of the evaporation of water. When repeated in a current of air, it was concluded that a constant temperature was reached at which all the oxygen absorbed was used to evaporate water. Therefore it was suggested that the heat of condensation of water could raise the temperature of a mass of coal to  $100^{\circ}\text{C}$ . If oxygen was then to reach the coal, it could evaporate all the condensed water together with its own combined water, after which it would start heating at an increasing rate.

Davis and Byrne<sup>19</sup> used a vacuum - jacketed tube, whose temperature was kept to within  $0.013^{\circ}\text{C}$  of the oil bath by a regulator. A beam of light reflected by the galvanometer varied the current of a selenium cell, which operated a relay system which controlled the heating.

Dried coals were exposed to dry air, and it was found

that the heating tendency of coal high in oxygen content was, in general, greater than those of low oxygen content. The minimum temperature above which spontaneous heating took place was found as follows: The temperature-time curve was fitted with an equation of the form:

$$\theta = \frac{K(a+T)}{b-T}$$

where  $\theta = ^\circ\text{C}$

$T = \text{hours}$

$$\frac{d\theta}{dT} = \frac{K(a+b)}{(b-T)^2}$$

for a coal whose  $a = -103$   
 $b = 61.74$   
 $K = 25.26$

the temperature when  $\frac{d\theta}{dT} = 0$  is  $\theta = K = 25.26^\circ\text{C}$   
 i.e. below this temperature no heating could occur. When  $T = 61.74$  hours, the coal fired. The heat loss by a spherical heap of coal was calculated, and the tendency of the heap to fire was evaluated.

More recently, Curdmore<sup>17</sup> used a copper constantan thermocouple to measure the temperature difference between the coal and the bath. The voltage was amplified and used to actuate the bath heaters by a system similar to that described above. The temperature difference was kept within  $0.1^\circ\text{C}$ .

### Effects of Moisture and Humidity

The effects of moisture transfer in the development of a heating is more important than has often been realised.

The experiments carried out by Winmill showed that the large amount of heat required to evaporate the moisture of coal greatly retarded the heating until the coal had become dry.

Davis and Byrne<sup>20</sup> used an adiabatic calorimeter described in the last section to measure the heating rate of coals at different degrees of drying treatment. The initial temperature was at 40°C and 70°C. The following conclusions were reached: Coals with moisture content "as received" would not heat in dry oxygen but dropped the temperature instead, owing to the evaporation of moisture.

Dried coal would heat spontaneously from 70°C. The rate of spontaneous heating of moist coal in moist oxygen was found to be dependent on the rate of flow of oxygen. At slow flows the rate of heating would be slower than with dry coal; at more rapid rates the coal cooled because of moisture evaporation. Therefore in a coalpile the hazard of spontaneous heating would be greatly reduced if the vapour pressure of the moisture in the coal was greater than that of the air with which it was in contact. Moisture would be evaporated and there would be cooling due to latent heat of evaporation. The latent heat more than counterbalanced the exothermic oxidation until the vapour pressure of water in the air and in the coal were in equilibrium.

Berkowitz and Schein<sup>3</sup> showed that the heat of wetting would raise the temperature of different types of coal at a much higher rate than that in the heating by oxidation. The limiting temperature rise in an adiabatically maintained fuel bed cannot exceed about 0.27°C/hr, by oxidation, at an initial temperature of 25°C, while the temperature rise when oxygen saturated with water vapour was passed through

a bed of dry coal at  $25^{\circ}\text{C}$  was from 0.30 to  $3.90^{\circ}\text{C}/\text{min}$  for different types of coal. At  $40^{\circ}\text{C}$  the rates were from 0.5 to  $6.7^{\circ}\text{C}/\text{min}$ . Therefore the heat of wetting might play an important role in starting a heating, and it remained large enough to influence the oxidation of any coal whose moisture content was below the equilibrium value. However most coals as mined contain their maximum moisture content, and before they can be further wet they must previously somehow have been dried in an inert atmosphere.

Stott<sup>92</sup> measured the heat of oxidation and drying of coal by an isothermal calorimeter. The heat changes caused by drying were much higher than those by oxidation. At the same flow of air, the heat produced by oxidation at  $40^{\circ}\text{C}$  was found to be 1700 cal/100 gm of coal after 40 hours, while the heat of drying was 5880 cal/100 gm of coal. It was concluded that heat transfer by evaporation must play an important part in the development of spontaneous heatings in coals having high initial moisture content.

Coal dried in vacuum was found to fire spontaneously in 30 min. from an initial temperature of  $22^{\circ}\text{C}$ , when oxygen saturated with moisture was passed through it, while dry oxygen caused the coal to fire in 12 hours from a temperature of  $18^{\circ}\text{C}$ <sup>93,94</sup>.

Experiments carried out by Hodges and Hinsley<sup>58</sup> also showed the same effect of the evaporation of moisture. It was found that when saturated oxygen was passed through dry coal initially at  $30^{\circ}\text{C}$ , the coal fired after 5 hours. When dry oxygen was passed through dry coal, the coal did not



fire. In subsequent investigations Hodges and co-workers<sup>59</sup>,  
60, 61, 4, showed the importance of humidity in the initial  
stages of the heating, and concluded that the danger of  
spontaneous heating became greater with the increase in the  
humidity of the air.

## 2. OXIDATION OF COAL

Coal absorbs gaseous oxygen to form an intermediate oxidation product in the initial stages of oxidation at low and moderate temperature. This compound, termed the coal oxygen complex, is formed by a chemical process, which has a nature similar to chemisorption. The oxygen molecule is bonded to the chemical structural unit (C-H) to form a hydroperoxide (C-O-O-H). The peroxygen decomposes rapidly at temperatures above 70°C to give carbon dioxide, water and carbon monoxide. The coal shows changes in susceptibility to further oxidation. If the oxidation is continued at higher temperatures, the organic material of the coal is converted into alkali-soluble products, which are the regenerated humic acids. Further oxidation will degrade the humic acids to the lower molecular weight, water soluble coal acids. At temperatures below 100°C, humic acids are not formed in any appreciable amount<sup>125</sup>.

The ratios CO<sub>2</sub> evolved/O<sub>2</sub> absorbed, and CO evolved/O<sub>2</sub> absorbed increase with temperature and time<sup>105,40</sup>. The weight of the coal has been found to increase during the first stage, up to 70°C, then decreases as the amount of carbon monoxide, carbon dioxide and intrinsic water released increased. As the temperature increases, the weight increases again, because of the stability of the products, and followed by the rapid decrease as the coal substance is incinerated<sup>65</sup>.

The rate of low temperature oxidation of coal depends on the type of coal, particle size, extent of oxidation,

temperature and oxygen concentration.

### Type of coal

The reactivity of coal decreases with rank. As the inherent moisture content and porosity decrease as the carbon content increases to a value near 90 percent, therefore the reactivity also increases with porosity and moisture content. However, the low reactivity of high carbon content coals indicates that the reactivity does not depend entirely on the availability of the pore surface.

Low rank coals, especially subbituminous coal, are therefore very susceptible to heating, however high moisture content lignites are not susceptible to heating unless dry.

### Particle Size

The rate of oxidation has been found to increase as the particle size decreases.

Winmill<sup>107</sup> showed that the rate was not simply proportional to the outer surface of the coal particles. As the difference in the rates of oxidation became less as time went on, it was concluded that the same total quantity of heat would be produced ultimately by the oxidation.

Scott<sup>79</sup> found that for sizes larger than 20 mesh, the initial rate was directly proportional to the superficial surface area, for smaller sizes, the rate increased more slowly than increase in surface area and reached a maximum when the particles are approximately 0.1 mm in diameter, beyond which further subdivision had no effect.

Elder et al<sup>78</sup> found the rate was approximately proportional to the cube root of the external surface area present.

Van Krevelen<sup>65</sup> stated that for particles of less than 1 mm in diameter, a fourfold increase in surface area increased the rate of oxidation by a factor of  $1\frac{1}{2}$ , whereas below 0.1 mm the rate became constant.

Carpenter et al<sup>9</sup> obtained the relationship that the rate was proportional to the cube root of the specific external surface. The external surface seemed to be but a small fraction of the surface accessible to oxygen. The internal surface was found to be independent of the particle size and could not be correlated to the change in reactivity. Therefore the accessibility of oxygen to the internal surface, carried out by transport processes, must be significant.

#### Extent of Oxidation

Using the results obtained by Graham, Winmill<sup>33,102</sup> and Schmidt and Elder<sup>78</sup>, Schmidt<sup>77</sup> found that the change of the rate with the amount of oxygen absorbed followed an equation of the type:

$$X = Ct^b$$

where  $X$  = oxygen consumed. Therefore the rate was

$$R = \frac{bC}{X^{1/b}} - 1$$

The constants  $b$  and  $C$  were found to be independent of the initial rate of oxidation, different types of coal, and were dependent on particle size. For  $\frac{1}{4}$ " coal,  $b = 0.8$  and  $C = 0.1$ , for - 200 mesh coal,  $b = 0.37$  and  $C = 0.5$ . Initially the rates for both fine and coarse coals are high. The rate decreases rapidly with fine coal, and becomes equal to that of coarse coal after seven days of oxidation. After 42 days,

both sizes will have consumed the same amount of oxygen.

### Temperature

The temperature dependent coefficient of the rate has been found to follow the Arrhenius equation. Schmidt<sup>77</sup> found that the activation energy of the rate when the coal has consumed 1 percent of its weight of oxygen, were of the order 25 Kcal/mole for temperatures above 85°C, and 16 Kcal/mole for temperatures below 84°C, from the data obtained by Graham<sup>33</sup> for coal size - 200 mesh. For coal of size -  $\frac{1}{4}$ " , Schmidt and Elder<sup>78</sup> found the value 11 Kcal/mole.

Oreshko<sup>73</sup> showed that the oxidation of coal consisted of 3 stages: up to 70 - 80°C the process was chemisorption, having an activation energy of the order 3 - 4 Kcal/mole. The decomposition of the complex was dominant at temperatures up to 130 - 160°C, the activation energy was 6 - 8 Kcal/mole. Chemical reaction took place at 180 - 290°C, and the activation energy was of the order 12-17 Kcal/mole.

Sebastian and Mayers<sup>80</sup> found the activation energy for the gross oxidation process as 30 Kcal/mole.

The activation energy has been found to increase with increasing degree of oxidation and temperature.

Scott<sup>79</sup> found that the rates obtained for anthracite were proportional to an exponential function of temperature, while lower rank coals showed better agreement with the Arrhenius equation. Yamasaki<sup>120</sup> obtained the relationship between the oxygen absorbed and the temperature as  $\ln X = bT + c$  for the range 30 - 100°C. From which it was suggested that physical absorption was predominant below 30°C, chemisorption

was the dominant process between 30°C and 100°C.

### Oxygen Concentration

Winmill<sup>107</sup> found that the rate of reaction of coals after exposure for 96 hours to a current of air at 30°C was proportional to the square root of the oxygen concentration for -60 mesh and -2+10 mesh sizes.

Schmidt and Elder<sup>78</sup> showed that for coals differing in rank and extent of oxidation, the rate of oxidation at 99°C was proportional to the 0.61 power of the oxygen concentration.

### Kinetics Study at Moderately High Temperatures

At temperature ranges from 150°C to 300°C, Georgiadis and Gaillard<sup>31</sup> found that the rate of oxygen consumed which was unrecoverable as gaseous product could be expressed by the relation:

$$\frac{dO_2(\text{bound})}{dt} = a - kO_2(\text{bound})$$

where  $a$  was a function of the transport processes in the gaseous and solid phase, temperature and type of coal. If the rate equation represented the consecutive formation - desorption of the oxygen coal complex, the decomposition of the complex was a first order reaction with respect to the amount of oxygen which was absorbed and fixed by the coal, independent of the nature of the coal, temperature and the transport processes.

The formation of the complex, which had the rate coefficient  $a$  was therefore a surface reaction. The activation energy of the process was found to be 6.5 Kcal/

mole and increased with increasing extent of oxidation. The higher values obtained by other investigators were based on the total oxygen consumed by the coal and therefore were the activation energy of the first reaction, that is the formation of the complex.

The oxidation at constant temperature progressed to a stage where the rate of decomposition of the complex was equal to the rate of formation. This stage was reached after 10 to 20 hours. The increase of the activation energy and the change of the ratio  $(CO + CO_2)/H_2O$  with the extent of oxidation showed that there was a continuous change in the processes which occurred in the oxidation.

#### Initial Stage of Low Temperature Oxidation

A kinetic study of the initial stage of the oxidation may show the nature of the absorption of oxygen, since the surface where the absorption takes place is readily available, and therefore the rate does not depend on other processes.

Wood<sup>122,123</sup> found that the rate can be expressed by the logarithmic rate equation:

$$\frac{dx}{dt} = Ae^{-Bx}$$

for the interval 25th - 175th minute of oxidation.

Sevenster<sup>82,83</sup> also found that the rate obeyed the logarithmic rate law in the first 10 to 15 minutes of the oxidation. It was suggested that even during this initial period, the transport processes might have a marked effect on the rate, since the activation energy passed a minimum value at 50° - 70°C, which was of the same order as that of the activated diffusion process. At higher temperature,

a chemical reaction might take place, as this was indicated by a high activation energy and an increasing rate of production of  $\text{CO}_2$ ,  $\text{CO}$  and water. In the intermediate stage, the transport processes in the macropores or those in the micropores might be the rate determining step. The oxidation finally reached a stage where simple diffusion, which was the slowest step, became completely rate-determining.

The nature of the diffusion processes in coal has been determined by Sevenster<sup>81</sup>. It was found that the diffusion coefficient was independent of pressure, and varied roughly as the reciprocal of the square root of the molecular weight, which, considering that the predominant pore size of coal was of molecular dimensions, suggested that gases were flowing mainly by effusion. For water vapour, oxygen and methane, surface flow was an important factor since these gases were strongly adsorbed to the surface. The process was therefore dependent on temperature, the activation energy was of the order 2 Kcal/mole.

Carpenter et al.<sup>9,10</sup> showed that the logarithmic rate law was followed in the first five minutes of the oxidation. The dependence of the activation of energy of the process on the size of the particles suggested that oxygen transport processes might also be involved in rate determination in the initial stage.

#### Heat of Oxidation

Lamplough and Hill<sup>67</sup> used an apparatus which allowed measurements of the rise in temperature and the oxygen absorbed by coal in a vacuum flask immersed in a constant temperature



bath to obtain values ranging from 2.8 cal/cc to 3.8 cal/cc of oxygen absorbed for different types of coal.

Winnill<sup>104</sup> used an adiabatic calorimeter to obtain a value of 2.1 cal/cc oxygen for Barnsley soft and hard coal.

Stott<sup>92</sup> used an isothermal calorimeter to measure the heat released by the oxidation of coal and found that the heat of oxidation was constant at different temperatures and extents of oxidation, and had a mean value of 3 cal/cc of oxygen absorbed.

## CHAPTER TWO

### ATTEMPTS TO PRODUCE SPONTANEOUS HEATING UNDER CONTROLLED CONDITIONS

When the heat of oxidation and heat of drying of fine sub-bituminous coal were measured at different temperatures, using an isothermal calorimeter, it was discovered that the heat required by the drying of moisture was much higher than that generated by the absorption.

It can be seen that heating is most likely to occur when the rate of heating is most rapid as this minimises heat transfer losses. To obtain a quick heating the oxygen supply to a pile should be increased by increasing the air current as the temperature rises and the rate of oxidation increases. However, this also increases the heat lost by evaporation and the rate of heating is determined by the interaction of these two effects. Experiments on spontaneous heating were therefore carried out by Stott<sup>93</sup>, with a stress on the role of humidity and moisture in the development of a fire.

Fresh coal was crushed and oxidised in a vacuum flask 8 feet long and 2 inches in diameter. Approximate calculations of the heat loss from the flask by conduction, radiation and sensible heat showed that the losses were negligible.

It was found that the rate of flow which gives the best rate of heating was about 100 cc/min when the air was saturated.

The temperature at the inlet region was found to be much reduced when the air was dry, but this decrease in temperature

was not found in further positions. It was thought that, because the rate of air flow was too small, the effect of evaporation was not prominent.

In the next experiment, coal which was already oxidised, and dried in vacuum for four days at  $95^{\circ}\text{C}$  was used. When air saturated at  $20^{\circ}\text{C}$  was passed through at 1000 cc/min, the coal attained a temperature which was higher than those attained by the oxidation of moist coal. The results showed the large quantity of heat generated by the wetting of dry coal.

Oxygen flow of 100 cc/min and air flow of 300 cc/min, was saturated at  $30^{\circ}\text{C}$ , were found to fire fresh coal, dried at  $105^{\circ}\text{C}$  in vacuum, in half an hour and 12 hours respectively. It was noticed that the portion of coal ignited was very localised, extended over not more than two or three inches. In practice it has also been found that the heatings are usually localised.

The oxygen absorption of coals from different mines were also measured.

The series of experiments showed the important role of moisture transfer in spontaneous heating. It also showed the possibility of studying small scale heatings in the laboratory. The mathematical equations which describe the development of heatings can therefore be checked and this leads to the possibility of relating the experiments to large scale heating.

The spontaneous heating of wool has been investigated by Walker et al. Experiments with an adiabatic calorimeter

have shown that the mechanism which is capable of causing fire in wool bales is oxidation. Heat due to other possible heating mechanisms, such as bacterial action and the heat of wetting, may raise the temperature to a point where the oxidation could become important<sup>110, 112</sup>.

The reactivity of wool was obtained from experiments in which the ambient temperature was kept constant. The temperature distribution was obtained from an approximate heat balance. The heat produced at the centre of the calorimeter was therefore obtained from the temperature rise. It was found that the rate of the wool - oxygen reaction is proportional to an exponential function of temperature, oxygen concentration, and its decrease is proportional to a power of the time of oxidation<sup>113, 116</sup>.

By evaluating the temperature distribution at increasing values of radius, the critical radius, beyond which ignition occurs, can be obtained<sup>114, 115</sup>.

An empirical equation of ignition, which takes into account the diminution of the rate of reaction with time, was derived<sup>120</sup>, and it was shown that the ignition of dry wool exposed to a flow of dry air in a constant ambient temperature, can be approximately predicted by the equation<sup>117, 112, 75</sup>.

Summarily, in some respects the data obtained by each investigator yielded consistent results. The reactivity of coal seems to conform to kinetic laws such as the Arrhenius equation, the logarithmic rate law, its change with the extent of oxidation can be correlated by a simple relation, and the

dependence of the rate of oxidation on the oxygen concentration is similar for each type of coal. The dependence of the rate of oxidation on the particle size can also be expressed by an approximate relation.

However, it cannot be said that for coals of similar ultimate and proximate analysis, their reactivity would be the same. For example, for coals of the same rank, Graham<sup>33</sup> found for coals of the Barnsley seam a rate of reaction of the order of 200 cc/100gm hr initially at 100°C, while Carpenter et al<sup>8</sup> found for a South Wales coal, a rate of the order of 35 cc/100gm hr at 95°C. The oxidation of the two coals have activation energy of the same order. Such difference in the reactivity shows that it is not possible to use data of previous investigators. Data obtained for New Zealand sub-bituminous coal indicate that it is much more reactive than those overseas, and the oxidation had an activation energy of the order of 39 Kcal/mole at temperatures up to 40°C, which is much more than the values found for coals in other countries. It is pointed out here that in New Zealand coals are much younger than those in some other countries such as Great Britain<sup>28</sup>.

Therefore, although much work has been carried out on oxidation, the oxidation characteristics of New Zealand coal can only be found by experiment, with only qualitative guidance from the results obtained in previous investigations for other coals.

As the complex process of heating can now be solved by numerical analysis, if the processes which occur are accurately described, the correct data are used for the heat and mass transfer processes, the effect of one process on the heating

can be studied accurately. Consider the processes which occur in the conditions which are favourable to a heating, the heat transfer processes and the molecular mass transfer process can be accurately described, and in controlled conditions, the process of moisture transfer can also be accurately described. Therefore the heat generation process, i.e. the oxidation, can be studied accurately in an experiment where the initial and boundary conditions are known and can be controlled. In the experiment the variables which the oxidation depends on, must change to an extent that can be accurately measured. It is then possible to obtain the effect of one variable on the oxidation in the heating by controlling the other variables, or if the effects of the other variables are known, because the effect of the heat generation process in the experiment can be accurately found. This type of experiment, which has been described above<sup>93</sup>, has an advantage in the study of the kinetics of oxidation, over the usual methods of measurements of oxygen absorption, in that it reduces the number of experiments needed to be carried out. Of course the processes have to be correctly described, and the measurement of temperature rise is not easy. However, this is a most fruitful method of studying a heating since the experiment is a small scale representation of what happens in practice, and the effect of moisture transfer cannot be accurately studied by any other method.

This thesis is concerned with a calculation procedure which can be applied to this experiment.

### CHAPTER THREE

#### PREVIOUS PUBLISHED CALCULATIONS

Computation of the heat transfer processes, taking into account the moisture transfer, have already been made<sup>71,97</sup>. The conditions of the pile in the calculations were that the size of the coal was naturally distributed below  $\frac{1}{4}$ " and the unidirectional air current flowed horizontally through the pile. The gaseous products were assumed to consist mainly of carbon dioxide, the evolution of carbon monoxide would be negligible. The rate of generation of carbon dioxide was

$$(\text{CO}_2 \text{ evolved} / \text{O}_2 \text{ absorbed}) = 1.0 - 2.4 \exp(-0.1366 \text{ O}_c - 0.00314 \text{ T})$$

where  $\text{O}_c$  = oxygen consumed cc/100 gm  
 $\text{T}$  = temperature  $^{\circ}\text{K}$

The rate equation was:

$$\frac{d\text{O}_c}{dt} = \frac{C_1(\text{T})}{(1 + C_2\text{O}_c)^n}$$

where  $C_1(\text{T}) = 1.445 \times 10^{13} \exp(-8572.3/\text{T})$

$$C_2 = 0.022$$

$$n = 0.895$$

The rate was assumed to be proportional to the square root of the oxygen concentration. The heat of oxidation was taken as 3 cal/cc  $\text{O}_2$ .

The flow of the gas was small so that it had no convective effects, i.e. the coal and the gas could be considered to be at the same temperature.

Saturation humidity was assumed to be reached by the air current at all temperatures below boiling point. Water produced by the oxidation had no effect on the flow since the gas was saturated with vapour. It could have an effect on the moisture content, however it was assumed that this effect was negligible. The heat of wetting was taken as the latent heat of water. Bound moisture was set at a value of 1 percent.

The energy equation in one dimensional case could be written as:

$$\rho_1 C_1 \frac{\partial T}{\partial t} = \frac{dQ}{dt} - L \rho_2 C_2 G \frac{\partial Y(T)}{\partial T} \frac{\partial T}{\partial x} - \rho_2 C_2 G \frac{\partial T}{\partial x} + K \frac{\partial^2 T}{\partial x^2}$$

where  $K$  = thermal conductivity

$\frac{dQ}{dt}$  = rate of heat generation by the oxidation

$\rho_1, C_1$  = bulk density and specific heat respectively, of the pile

$\rho_2, C_2$  = density and specific heat respective of the air

$L$  = latent heat

$G$  = volumetric flow rate

$Y(T)$  = absolute humidity

The equations were solved numerically.

It was found that oxidation occurred mostly near the inlet surface of the heap. The distance that oxygen could reach into the pile depended on the magnitude of the flow and the rate of oxidation of the reacting region. The heat of oxidation at this region raised the temperature of the coal



and evaporated moisture to saturate the gas. As the saturated air reached further into the heap, water condensed from the air and the condensation raised the temperature of the coal to near boiling point. It could be seen that as the oxidation went on, the region where the condensation took place, receded further and further into the pile. The condensation brought the temperature of the coal to the highest temperature in the pile, and this region therefore, had the maximum moisture content. Temperatures near boiling point of water were reached within 4 - 5 days. Air currents of the order  $3 - 4 \text{ ml/cm}^2 \text{ min}$ , were found to give the most rapid temperature rise.

The lowest moisture content reached by the evaporation was found to be near 7 percent, before the oxidation rate diminished with the extent of oxidation, so that there was not even enough heat produced to maintain the temperature of the coal to evaporate the rest of the moisture.

Therefore, the results showed that besides oxidation, moisture transfer was an important process in the development of a fire. One of the most important features of this work was that no temperature above  $100^\circ\text{C}$  could be reached as the heat of oxidation was not sufficient to evaporate all of the water in one region.

As a fire was unlikely to occur under the assumed mechanism, the following suggestions were made for further investigations:

- Drainage of water may be an important factor.
- Moisture content - vapour pressure equilibrium curves for  $100^\circ\text{C}$  and above would be required. Accurate drying data would be needed for the calculations when the coal reaches low moisture contents. Mass transfer in the

solid phase might have to be considered.

- More accurate expressions for constants might have to be used, such as the heat of drying or wetting might be expressed as a function of moisture content.
- As the rates of the air current which gave the most favourable conditions for the possibility of a fire being developed were low, diffusion would have to be considered.

Investigations of these problems are the major topics discussed in this thesis. It is shown below that if the vapour pressure of water in the voids in the heap is made to be dependent on the moisture content of the coal in accordance with published data, then the calculations describe more accurately the spontaneous heating process and predict the occurrence of fire.

## CHAPTER FOUR

### CONSIDERATIONS ON MOISTURE CONTENT - VAPOUR PRESSURE RELATIONSHIP, DIFFUSION AND THE PERFECT GAS LAW

From the results obtained previously by Stott and Murtagh, it was shown that when the evaporation of moisture has been completed to a certain degree, the oxidation which generates heat to evaporate the moisture, is not capable of sustaining the drying because its rate is reduced by the extent of oxidation to below the value which is required to saturate the air to saturation humidity, and the temperature therefore starts to fall. Consider the oxidation of coal; when the coal has been oxidised for some hours in the temperature range around  $70^{\circ}\text{C}$  and higher, the oxidation at lower temperatures will be practically extinct. Therefore although the heat required/unit time by the evaporation at lower temperatures will be reduced exponentially with temperature, the rate of oxidation is reduced at a faster rate, and the temperature must in time fall to that in equilibrium with the inlet air current. As long as the oxidation and evaporation can continue at temperatures of  $70^{\circ}\text{C}$  and higher, the total heat generated will be sufficient to evaporate all 20 percent moisture content. At lower temperatures the total heat generated by oxidation is not sufficient to evaporate all the moisture content. Therefore the evaporation of moisture can only be completed in the range of  $70^{\circ}\text{C}$  and higher temperatures.

Consider the vapour pressure - coal moisture content relationship. The vapour pressure, which is in equilibrium with a low moisture content, may be low enough so that its equilibrium condition can be sustained by the oxidation. Under

this condition, the processes of drying and oxidation will continue in the temperature range  $70^{\circ}\text{C} - 80^{\circ}\text{C}$ . The rate of oxidation will continue to be reduced by the extent of oxidation, but the equilibrium humidity will also be continuously reduced because of the reducing coal moisture content. Therefore it is possible that the equilibrium state can be retained until all the moisture has been evaporated.

However, if the equilibrium humidity is not low enough to be sustained by the oxidation, the temperature will start to fall as in the case when saturation humidity was assumed. In this case, the coal cannot fire by the process of oxidation alone (see Appendix 6 for a more detailed discussion). External causes must be an essential contribution to the heating. The fall of roof stone, which usually occurs after the fall of coal, can raise the initial temperature of the coal by the frictional heat from the fall. The finely divided fusain, which also has often been found at the site of the fire, has a rate of oxidation which is considerably higher than that of slack coal, because of its fine size.

Diffusion of the gases in the voids and the correction for the perfect gas law, should be considered at very low rates of air leakage. However, at higher rates of air leakage, diffusion and the perfect gas law may still have to be considered. From the gradients of the temperature curves, it will be shown that the diffusion of humidity can be considerable. Consider the fact that the heat of oxidation may just be adequate to finely balance the evaporation of moisture, the effect of these corrections can be the critical factor. Unless

it is shown that there is not a critical state, i.e. the equilibrium vapour pressure is well below the highest value which can be sustained by the oxidation, or that due to the nature of the heating, the overall effect of diffusion and the perfect gas law is negligible.

The factors pointed out here will be investigated in this thesis, so that their effect on the heating will be determined within the accuracy of the data available.

Diffusion is included in the equation of continuity for each component in the gaseous mixture. The equation is as follows:

For component  $i$

$$\frac{\partial}{\partial t} (\rho_i w_i) = - (\nabla \rho_i w_i \underline{V}) + (\nabla j_i) + r_i$$

where  $\rho_i$  = density  
 $w_i$  = mass fraction  
 $\underline{V}$  = inlet velocity  
 $j_i$  = diffusional flux  
 $r_i$  = rate of mass change

The perfect gas law gives:

$$\frac{\partial \rho_i}{\rho_i} = - \frac{\partial T}{T}$$

$$\frac{\partial \underline{V}}{\underline{V}} = \frac{\partial T}{T}$$

Where  $T$  = temperature

the energy equation is

$$C_1 \rho_1 \frac{\partial T}{\partial t} = K \nabla^2 T - C_2 \rho_2 \underline{V} \nabla T + \frac{dQ}{dt} - \Delta H_{H_2O} r_{H_2O}$$

Where  $\rho_1$ ,  $C_1$  = bulk density and specific heat respectively  
of the pile

$\rho_2$ ,  $C_2$  = density and specific heat respectively of  
the gaseous mixture

$$\rho_2 = \sum_i \rho_i w_i$$

$$\frac{dQ}{dt} = \text{heat generation term}$$

$$K = \text{thermal conductivity}$$

$$\Delta H_{H_2O} = \text{latent heat}$$

The rates of mass change for oxygen and carbon dioxide are evaluated from the rate equation and the formula to evaluate the ratio  $CO_2$  evolved/ $O_2$  absorbed, respectively. The humidity change term  $r_{H_2O}$  at low temperatures is evaluated by assuming saturation, if the moisture content change was negligible and can be considered to remain at saturation point. Therefore,

$$r_{H_2O} = \sum \rho_2 \frac{\partial Y(T)}{\partial T} \frac{\partial T}{\partial x} - \nabla j_{H_2O} + \frac{\partial}{\partial t} (\rho_{H_2O} w_{H_2O})$$

At high temperatures, the moisture content - humidity curves are used (see Appendix 5), therefore the term  $r_{H_2O}$  is evaluated from the change in humidity at each point.

The diffusion flux is:

$$j_i = D_{im} \nabla (\rho_i w_i)$$

where  $D_{im}$  = effective binary diffusivity of component  $i$

$$= \frac{1 - w_i}{\sum_{j \neq i} \frac{w_j}{D_{ij}}}$$

It is pointed out here that at high temperatures, the

dominant terms in the energy equation are the heat of reaction and the heat due to moisture transfer. Therefore the equation can be considered as consisting mainly of:

$$C_1 \rho_1 \frac{\partial T}{\partial t} = \frac{dQ}{dt} - \Delta H_{H_2O} r_{H_2O}$$

## CHAPTER FIVE

### EXPERIMENTAL WORK

The work discussed earlier in the thesis has shown the possibility of carrying out the oxidation of coal under conditions which would allow spontaneous heating in the laboratory.

The accuracy of the equations which have been used to describe the process of heating can therefore be determined by comparing the computed results with those obtained from an experiment.

Therefore experiments on oxidation of coal by an air current have been carried out, with the following aims.

The rise in temperatures, and the oxygen absorption should be large enough to be measured with reasonable accuracy. The changes in variables such as oxygen concentration, humidity along the direction of flow of the air current should be adequate to have an appreciable effect on the heating.

Data from such an experiment would allow an assessment of the accuracy of the computations.

Measurements of the heat of and rate of oxidation and heat of wetting, are also needed for coal particles of sizes up to  $\frac{1}{4}$ ". Relationships which relate the rate of oxidation of coals of different sizes have been given in literature, however they are most probably only correct for the coals which were used to obtain the relationships. Data for New Zealand coal, which is used in the experiments, have been obtained for - 72 + 200 mesh sizes only.



A summary of the experimental work and computations is given below.

(i) Experiments on low temperature oxidation of coal.

(ii) Basing the calculation on the original program developed by Stott and Murtagh, it was attempted to solve the energy equation by solving the set of simultaneous equations resulting from the finite difference approximations of the energy equation. The method proved to converge fast enough and gave results which were similar to that of the above-mentioned program.

(iii) An unsuccessful attempt was made to measure oxidation rates for New Zealand coals.

(iv) The program developed in (ii) was applied to the oxidation in the column and it was found that the radial heat conduction was important. Therefore the energy equation in cylindrical coordinates was developed and used to take into account this effect.

(v) A solution including the effects of diffusion of gases was developed and included in the program. The effect of the perfect gas law was also included (i.e. change in gas volume with temperature).

(vi) The program for the one dimensional case, taking into account the moisture content - vapour pressure relationships was then developed. This program was also used to determine the effect of the inclusion of the perfect gas law and diffusion.

The programs for (iv) and (v) are described in appendices 2 and 3 and shown in Figure 50. The program for (vi) is described in appendix 4 and shown in Figure 51.

NOTE. The effect of gas diffusion can be included by using subroutine PSB as described in appendices 3 and 4.

### Low Temperature Oxidation Experiments

A column was constructed from 5 ft. sections of 10 cm diameter glass tubing (Figure 1). The column was covered with polystyrene foam sections, of outer dimension 18" x 18".

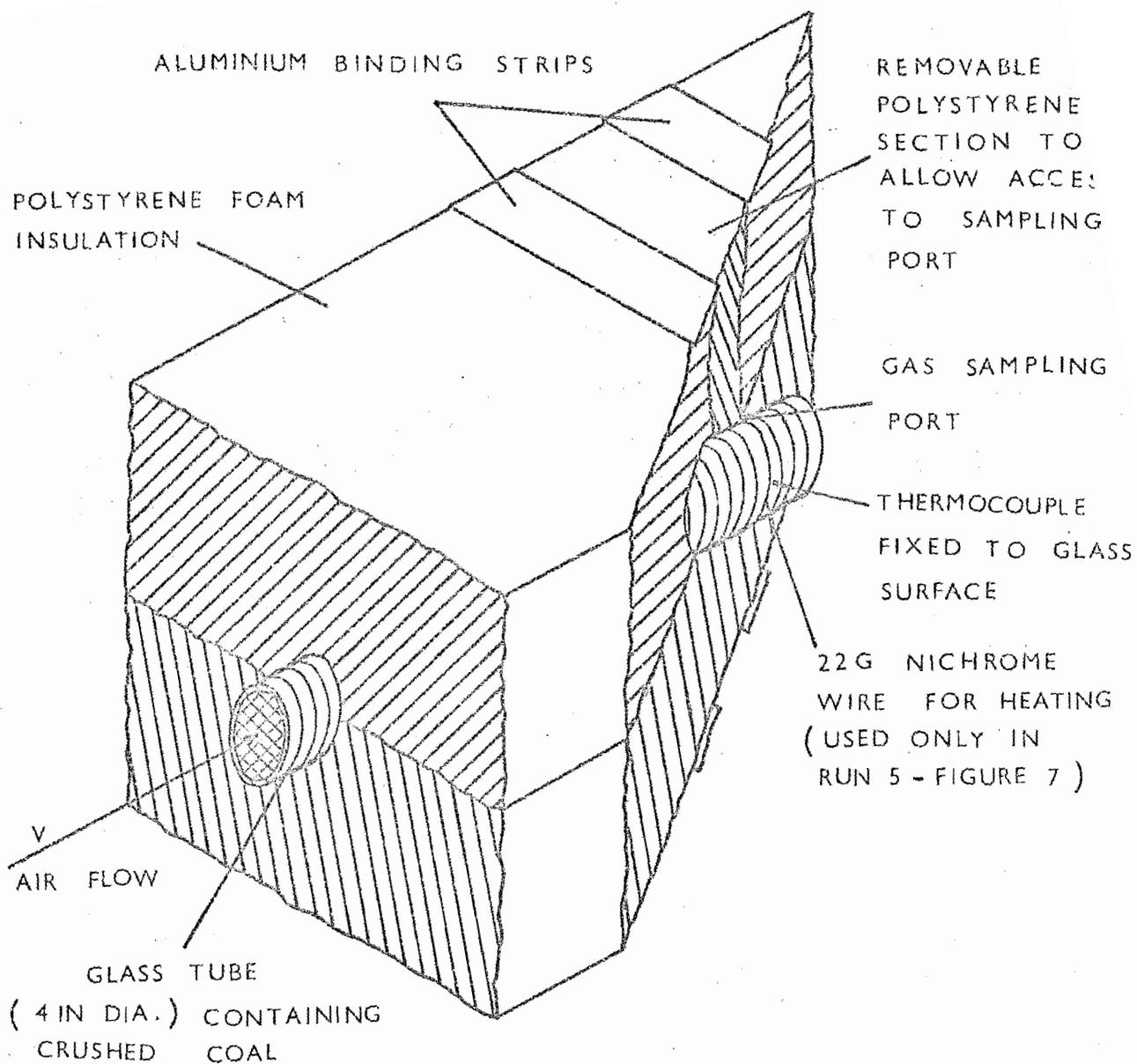
A heater system was cemented on to the glass tubes. Sampling points and thermocouple junctions were placed at 2 or 3 ft. intervals.

The column was supported at an inclination to aid the loading of coal into the column. It was set up in a room whose temperature was kept at a constant value  $\pm 1^{\circ}\text{C}$ .

Fresh coal was crushed in a jaw crusher, passed through a  $\frac{1}{4}$ " sieve, and loaded into the column as quickly as possible, i.e. within  $\frac{1}{2}$  an hour. When the column was full, nitrogen saturated with water vapour was passed through the column, and the column of coal was allowed to reach room temperature. When the nitrogen flow was stopped, a current of air was passed through the coal to flush out the nitrogen. The air flow then was lowered to the desired value and the oxidation then began.

The inlet flow of air was measured by a rotameter. The humidity of the outlet gases was measured by a drying tube, the carbon dioxide evolved was found by absorption by a sodalime - anhydrous tube, the oxygen concentration was measured by a Beckman paramagnetic oxygen analyser, and the carbon monoxide content was measured by a Drager colorimetric tube apparatus.

Gas analyses at the sampling points could be carried out frequently only when a gas chromatograph was available, as gas



COAL ANALYSIS			
PROXIMATE ANALYSIS	ANALYSIS	ULTIMATE ANALYSIS	ANALYSIS
	% WEIGHT		% WEIGHT
MOISTURE	20	CARBON	75
VOLATILE MATTERS	36	HYDROGEN	5.4
FIXED CARBON	39	NITROGEN	1.1
ASH	5	OXYGEN	18.5

FIGURE 1B. DETAILS OF THE COLUMN AND COAL ANALYSIS

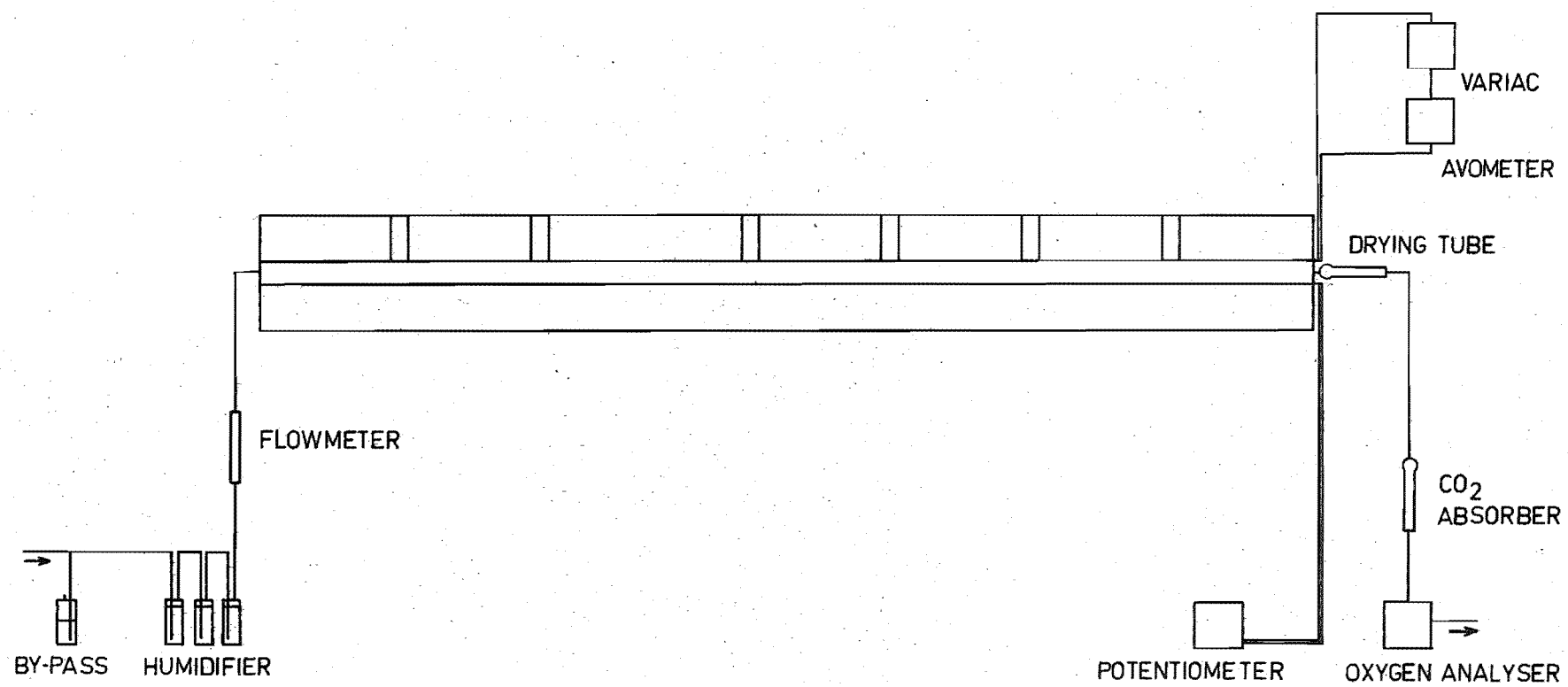


FIGURE 1. LOW TEMPERATURE OXIDATION APPARATUS

analyses by other methods required large samples. A gas chromatograph column for the detection of water vapour was not available at the time the experiments were carried out, therefore it was not possible to measure the humidity at each sampling point.

The temperature measurements were carried out by using either recorders or a potentiometer.

As much data as possible was obtained during the first 4 - 5 hours of a run, and at hourly intervals afterwards. The experiment was stopped when the temperatures at all points were decreasing. The results are shown in Figures 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 and Table I.

#### Heat of Oxidation Experiment

To provide the kinetic data for the interpretation of the results obtained from the above experiments, the rate and heat of oxidation at different values of the variables on which the oxidation is dependent, i.e. temperature, particle size and oxygen concentration, must be obtained. Therefore following the above experiments, an attempt to measure the rate and heat of oxidation was made.

The heat produced by oxidation of  $\frac{1}{4}$ " coal would be very small, therefore the measurement requires a sensitive system. A constant temperature bath was constructed for the isothermal calorimeter which was used for the measurement. The temperature of the bath was controlled by a temperature controller using a thermistor as the sensor (Figure 2).

A fresh lump of coal at least 4" in diameter was broken, its central part was crushed and the coal was placed into a

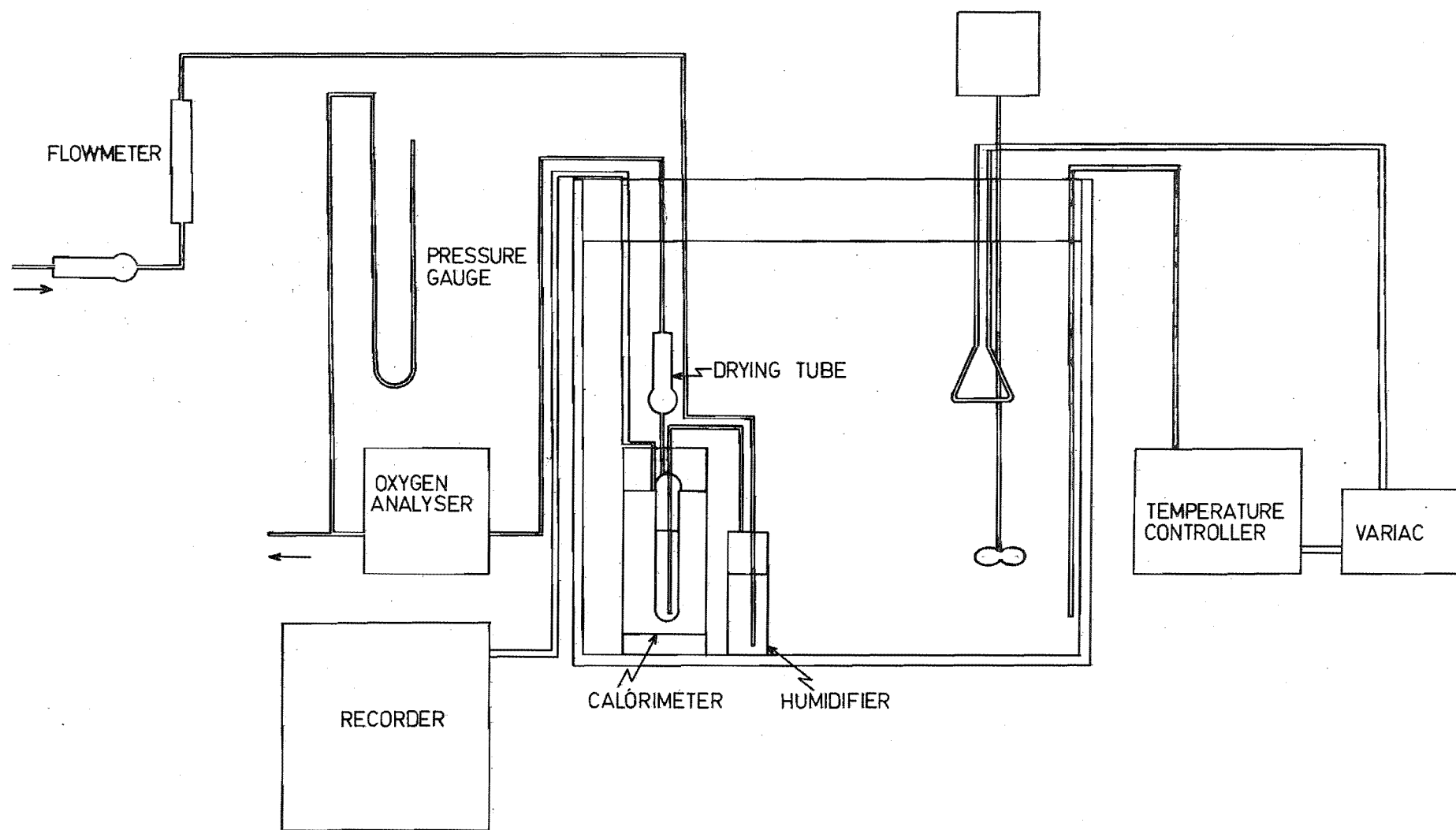


FIGURE 2. HEAT OF OXIDATION APPARATUS

glass container. The glass tube was weighed and quickly placed inside the calorimeter. The calorimeter, humidifier trains, and the drying tube to measure the humidity of the outlet gas was placed into the water bath. A flow of nitrogen passed through a pyrogallol solution, saturated by the humidifier trains, was allowed to run through the coal sample. The heat output measured by the calorimeter indicated that the moisture content of the coal had reached its equilibrium value when it reached a zero value. The nitrogen flow was stopped, the nitrogen left in the system was flushed out by a current of air. A measured current of air, saturated with water vapour was then passed through the coal sample. The outlet humidity was determined by the drying tube, the oxygen concentration was measured by a Beckman oxygen analyser. Pressure difference between the atmosphere and inside the calorimeter was measured by a water manometer.

However, it was found that the pressure loss by the hypodermic tubing, which was used for inlet and outlet from the calorimeter, caused the air to become unsaturated at the pressure inside the calorimeter. The hypodermic tubing was used to reduce the heat conduction from the coal sample to a minimum. The pressure change, beside causing evaporation of moisture of coal, had a cooling effect by expansion which was of the same order as the heat produced by oxidation. After futile attempts to improve the system, the test had to be abandoned (Appendix 1).

To produce a full set of heat and rate of oxidation data, in the range 20 to 100°C, was beyond the scope of this work and further experiments were not attempted.

### Oxidation Experiment

Following the above experiment, an attempt to measure the rate of oxidation was carried out. The measurements were also nearly as time-consuming as the above experiment, and the possibility of using this apparatus to measure a small change in the oxygen concentration has never previously been tried out. Therefore this experiment was mainly to find whether it was possible to measure the rate of oxidation by the equipment, and if possible to obtain some idea on the rate of oxidation at low temperatures of the coal used in the experiment.

A coal sample was placed inside a test tube. The flow of air into the test tube was measured by a soap bubble flow meter and the outlet oxygen concentration was measured by an oxygen analyser (Figure 3). The results are shown in Figure 14.



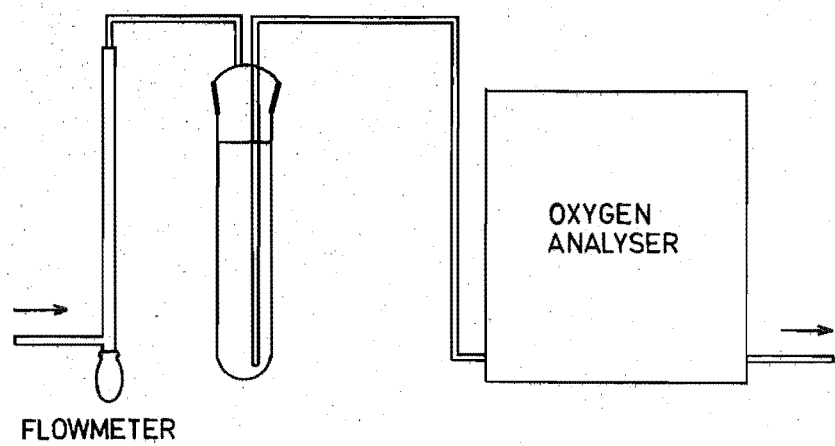


FIGURE 3. OXYGEN ABSORPTION APPARATUS

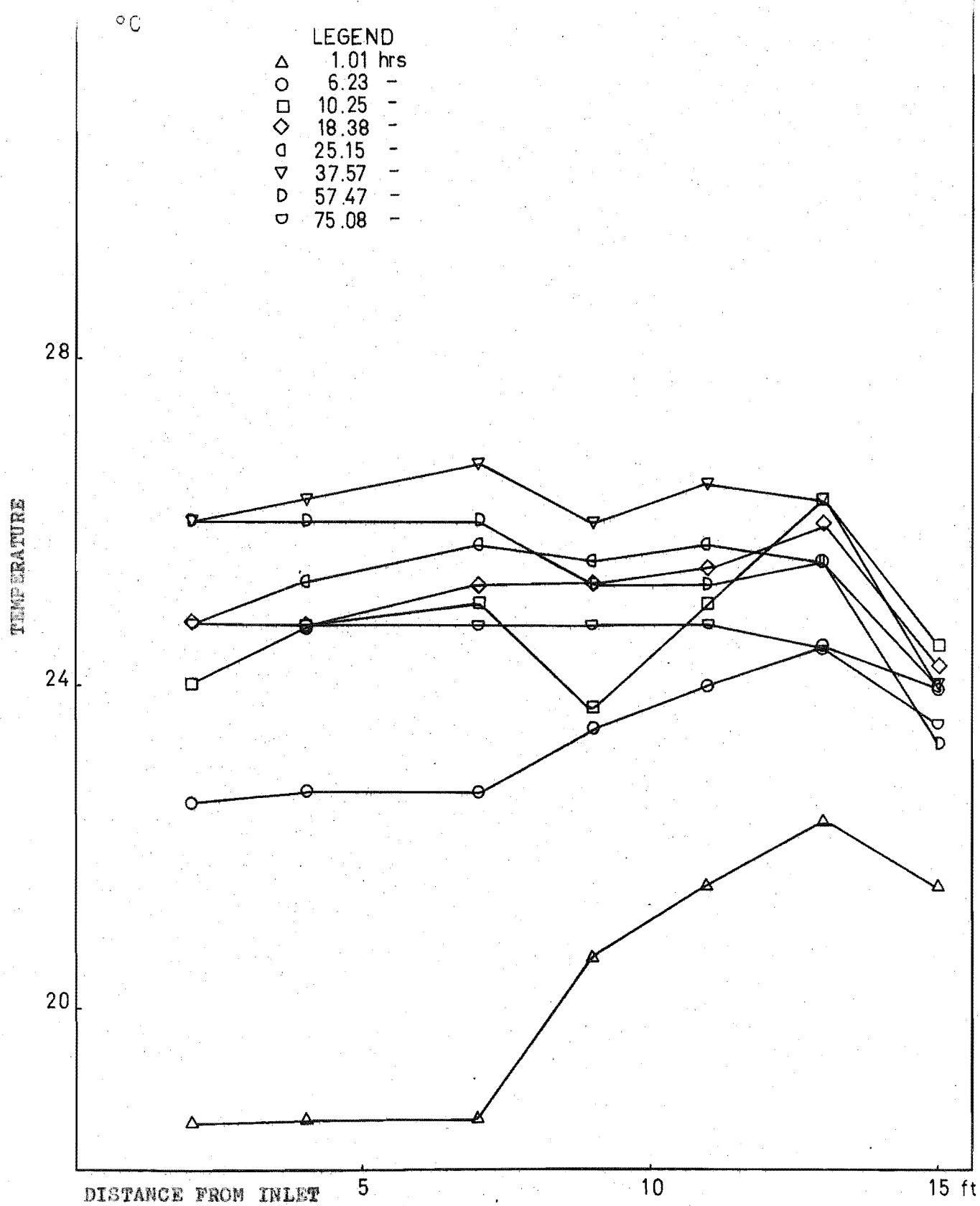


FIGURE 4. TEMPERATURE - RUN 1 - SPOILT

100-101000

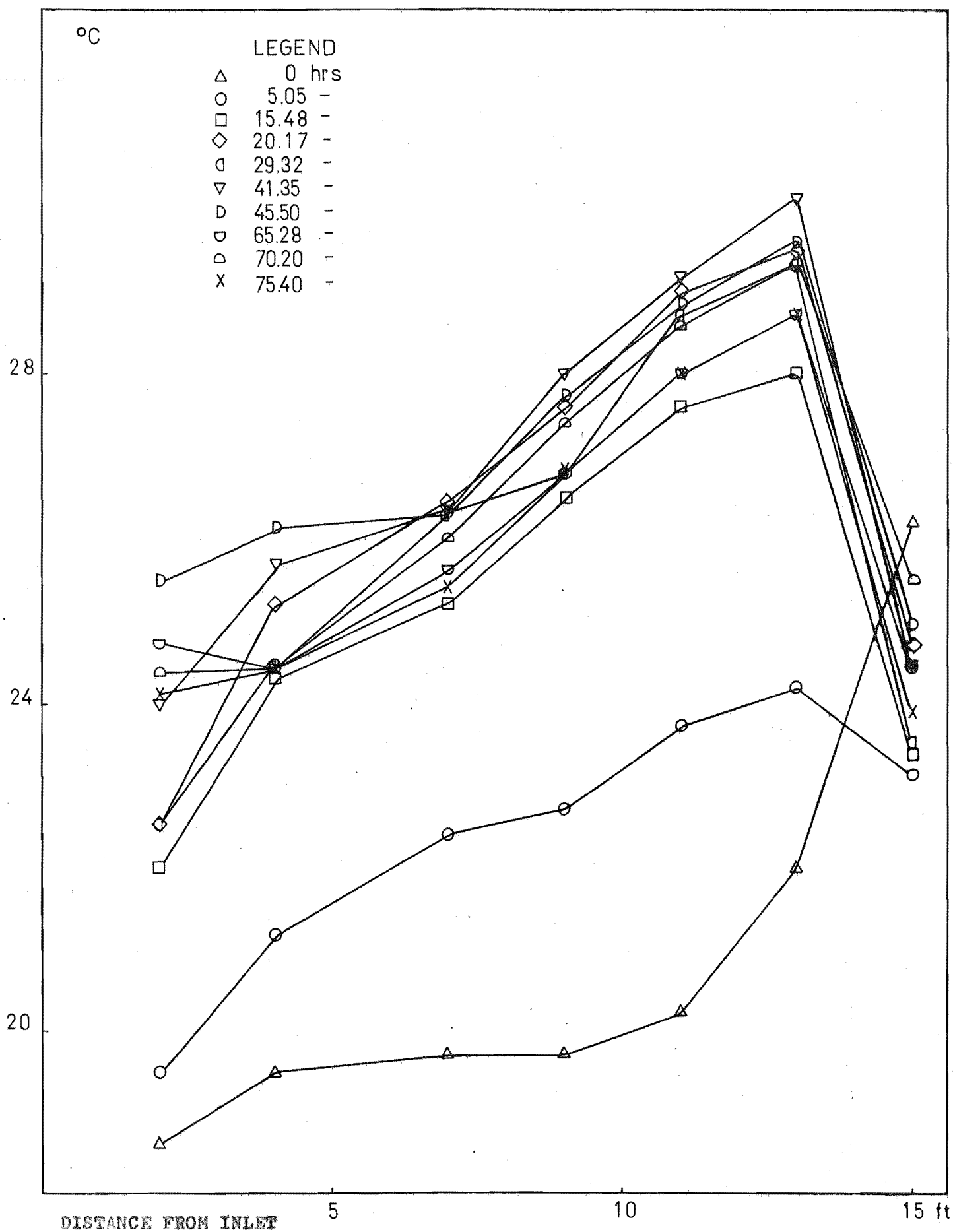


FIGURE 5. TEMPERATURE - RUN 2

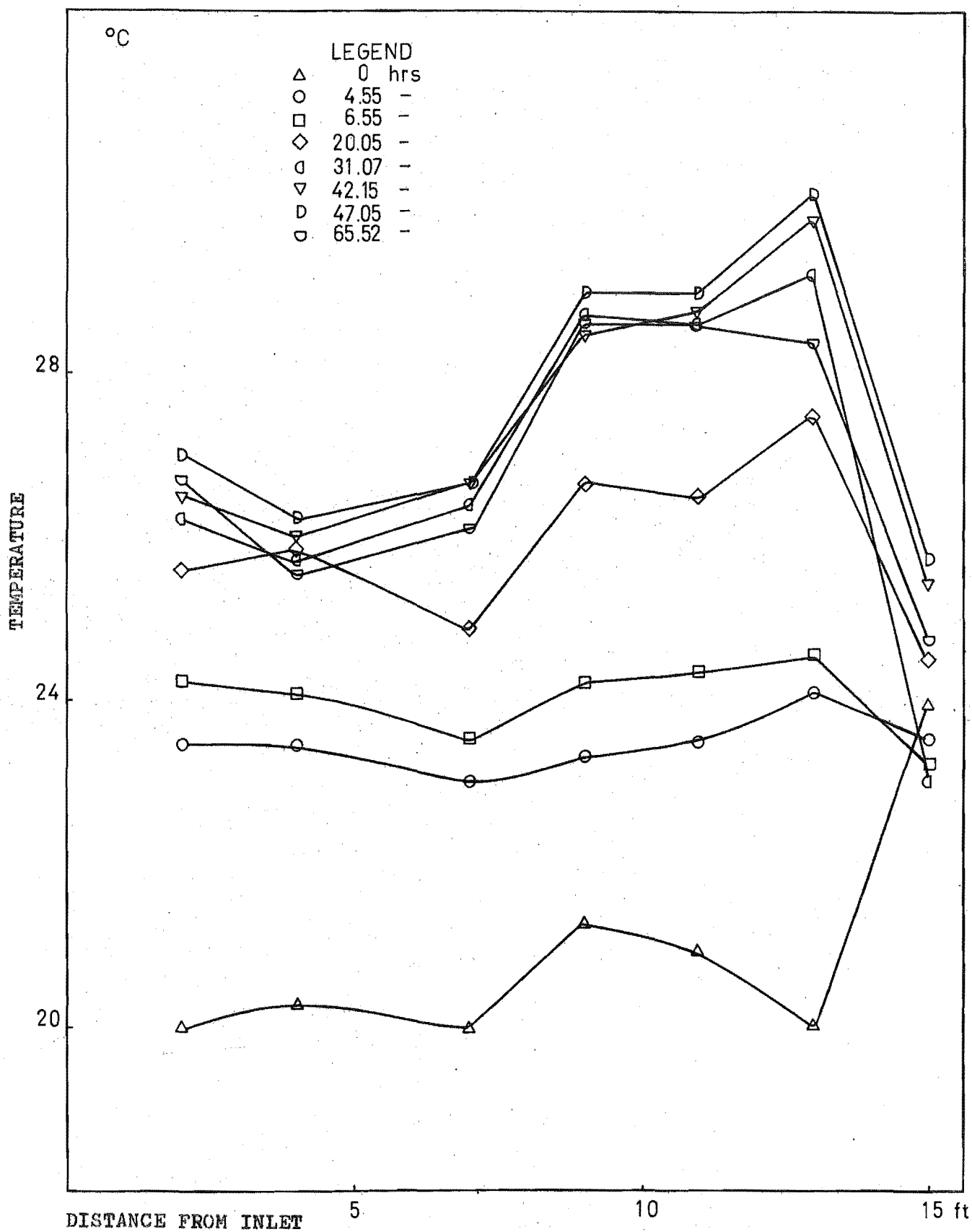


FIGURE 6. TEMPERATURE - RUN 4

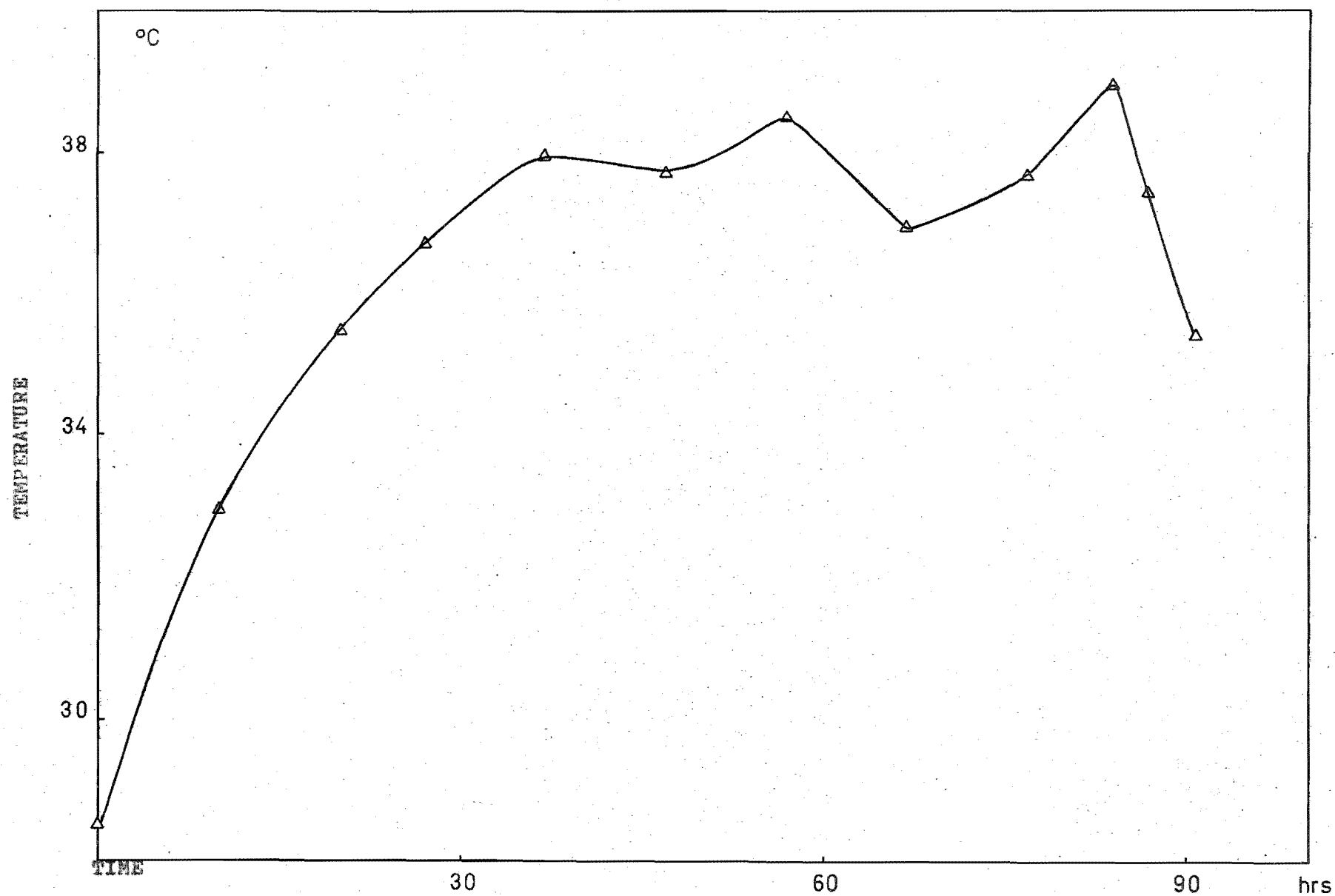


FIGURE 7. TEMPERATURE, 6 FT FROM INLET - RUN 5  
RATE OF FLOW .9 CC/CM<sup>2</sup> MIN, AMBIENT TEMPERATURE 35 °C

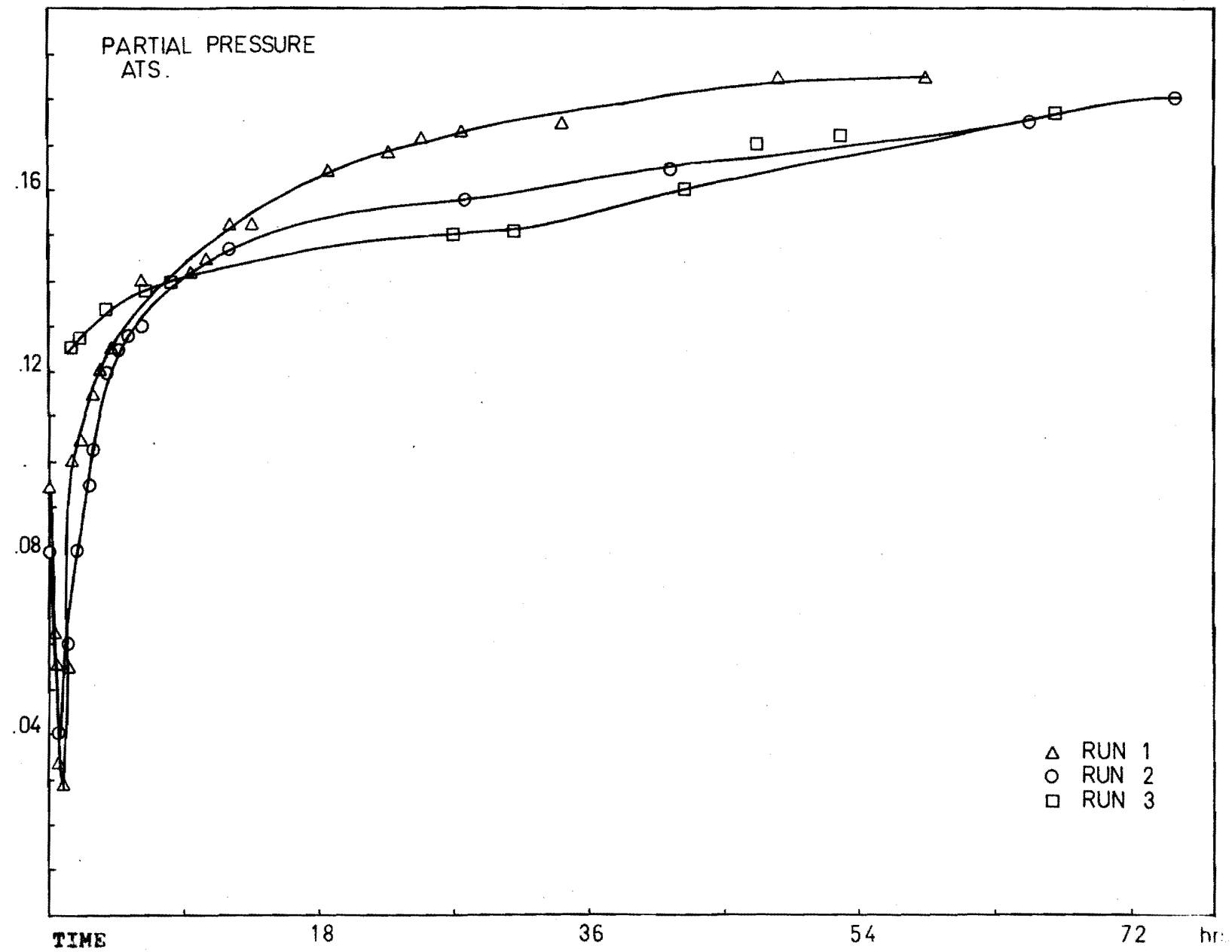


FIGURE 8. OUTLET OXYGEN CONCENTRATION

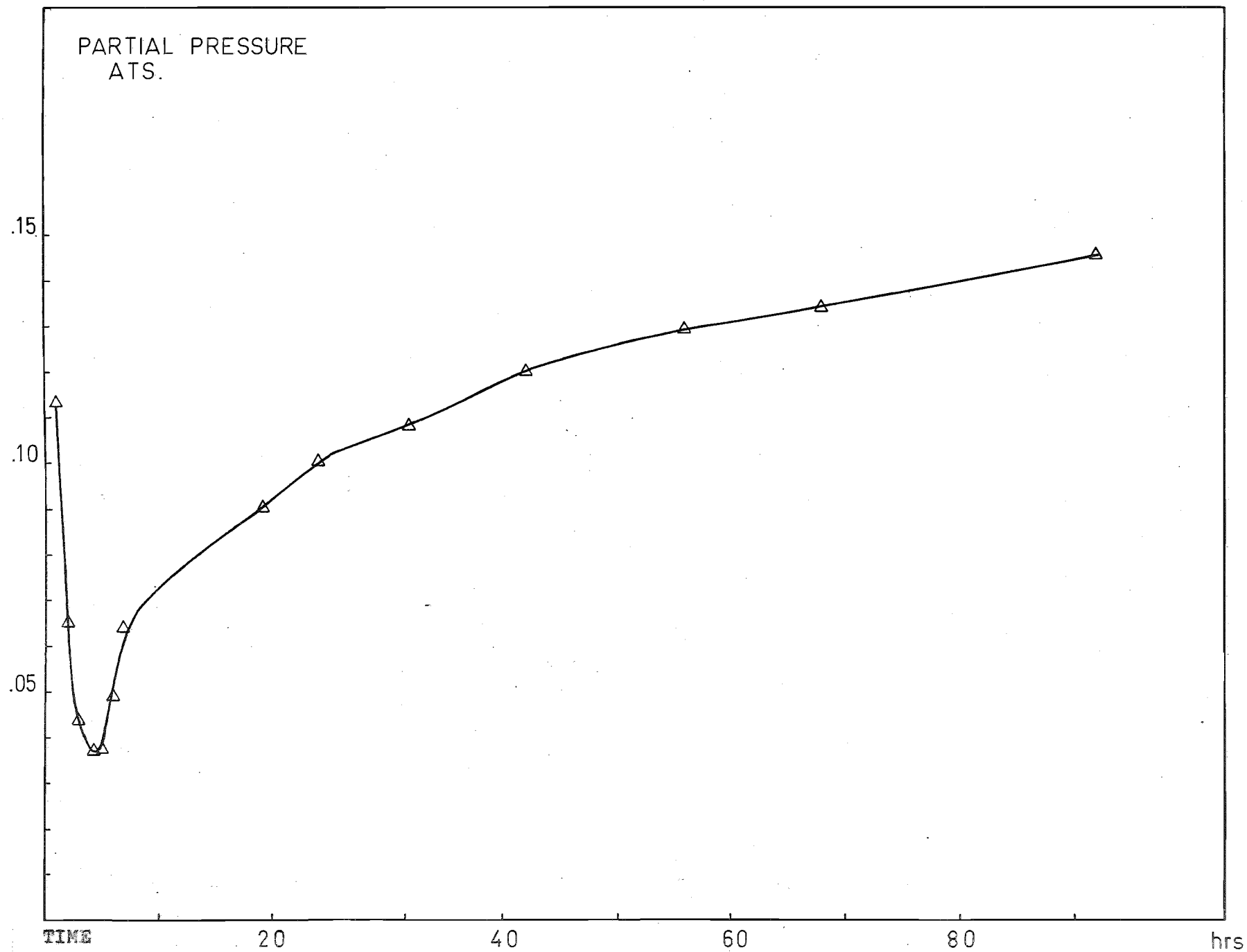


FIGURE 9. OUTLET OXYGEN CONCENTRATION - RUN 5

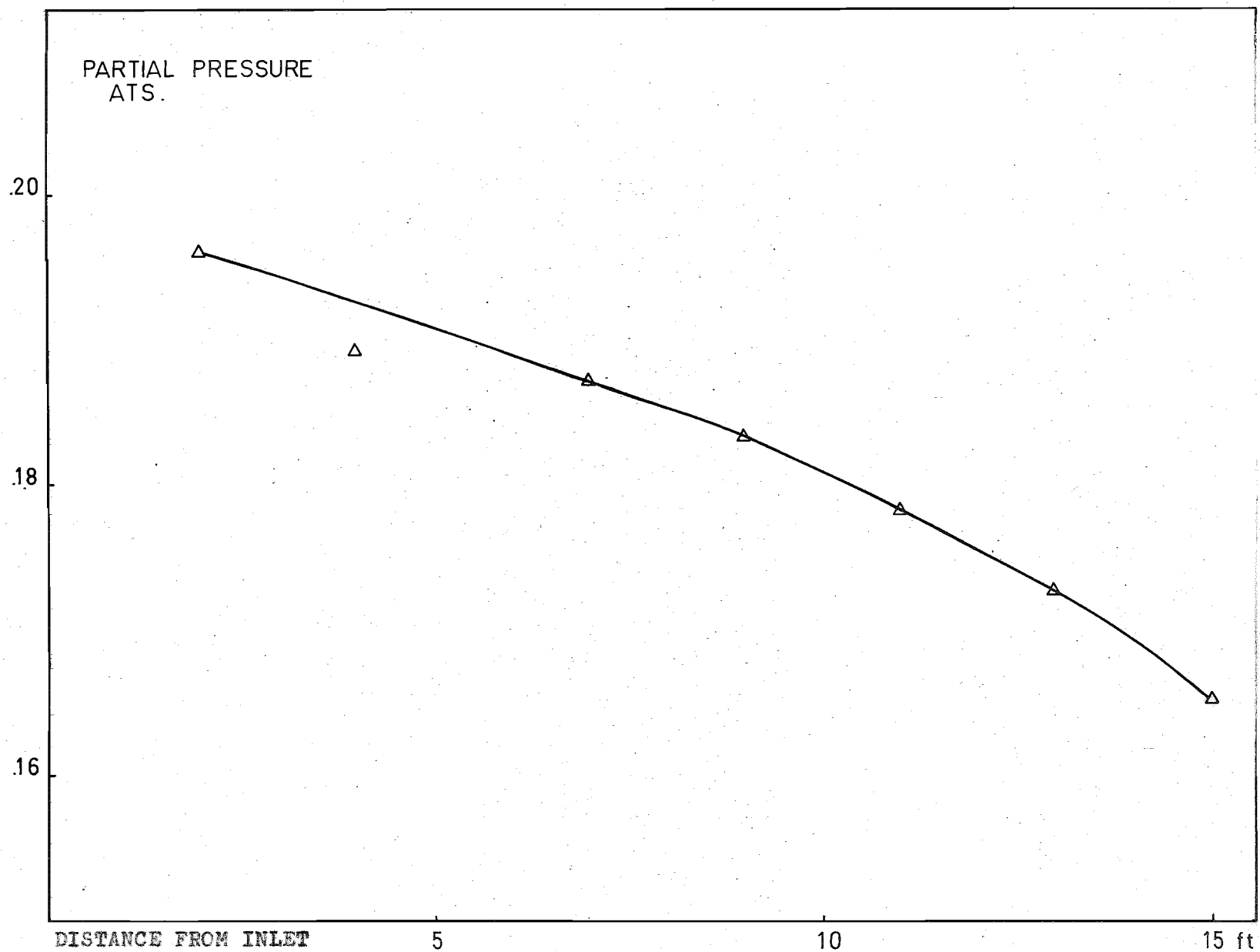


FIGURE 10. OXYGEN CONCENTRATION (OBTAINED BY GAS CHROMATOGRAPH)



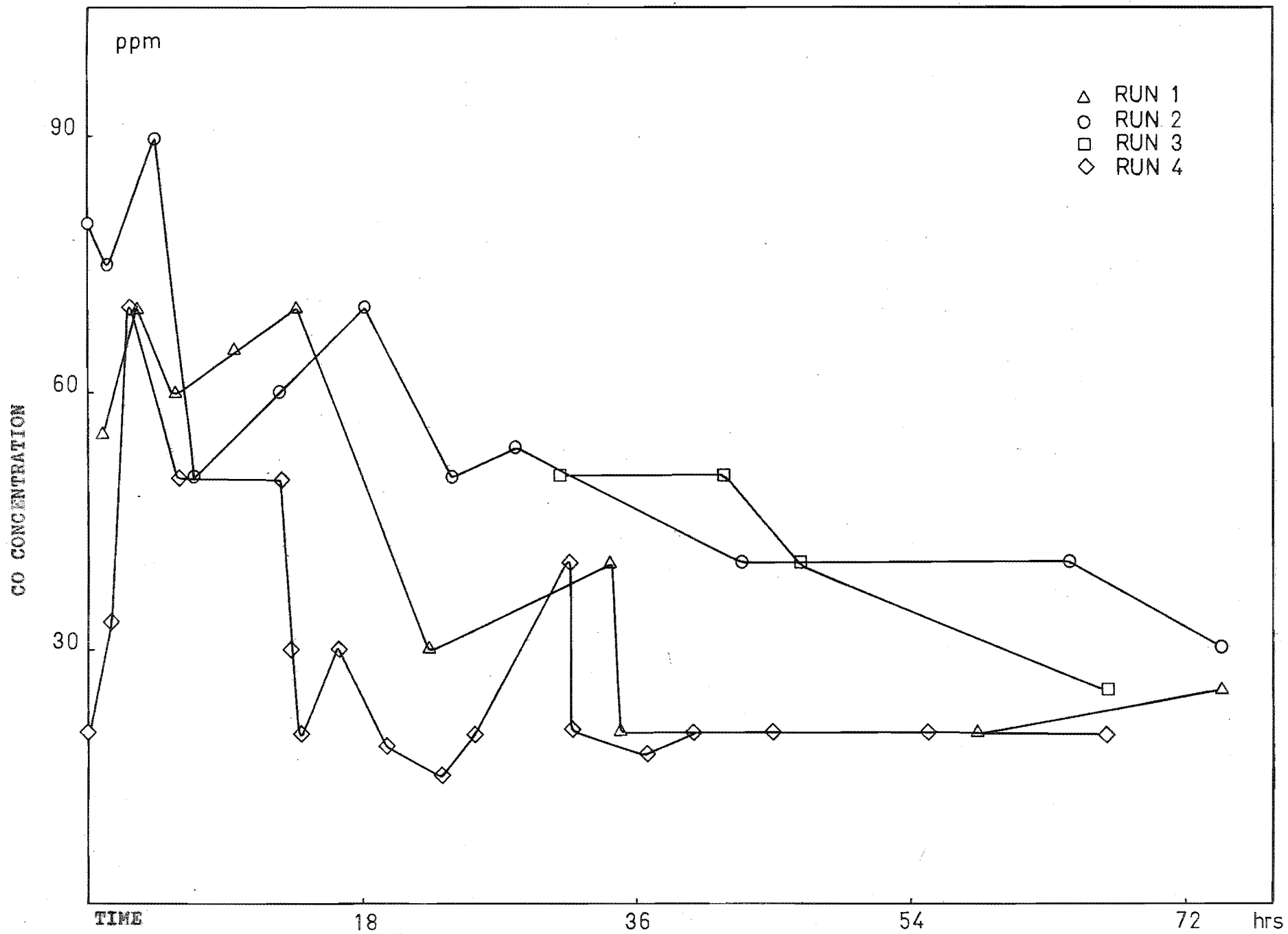


FIGURE 11. OUTLET CARBON MONOXIDE CONCENTRATION

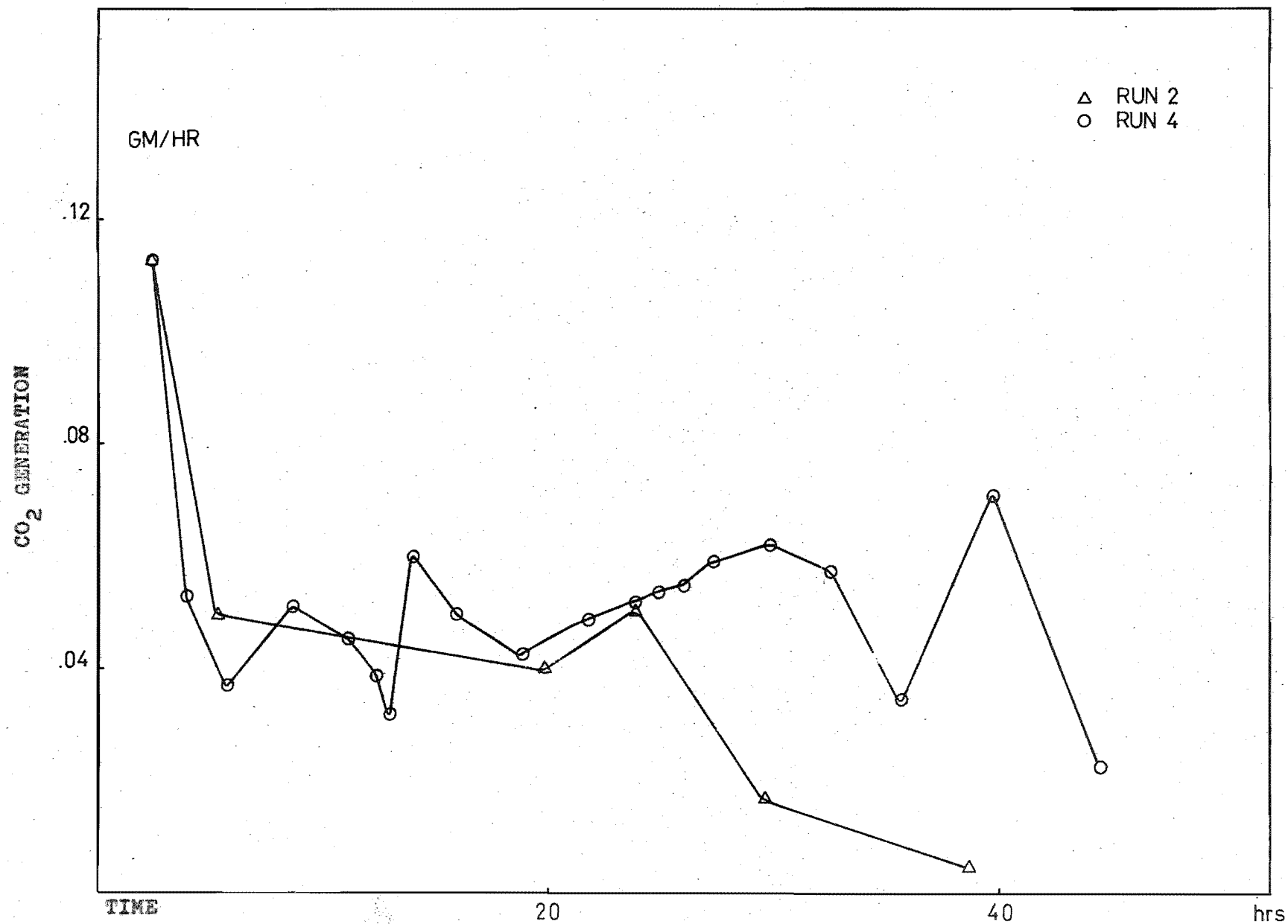


FIGURE 12 . CARBON DIOXIDE GENERATION

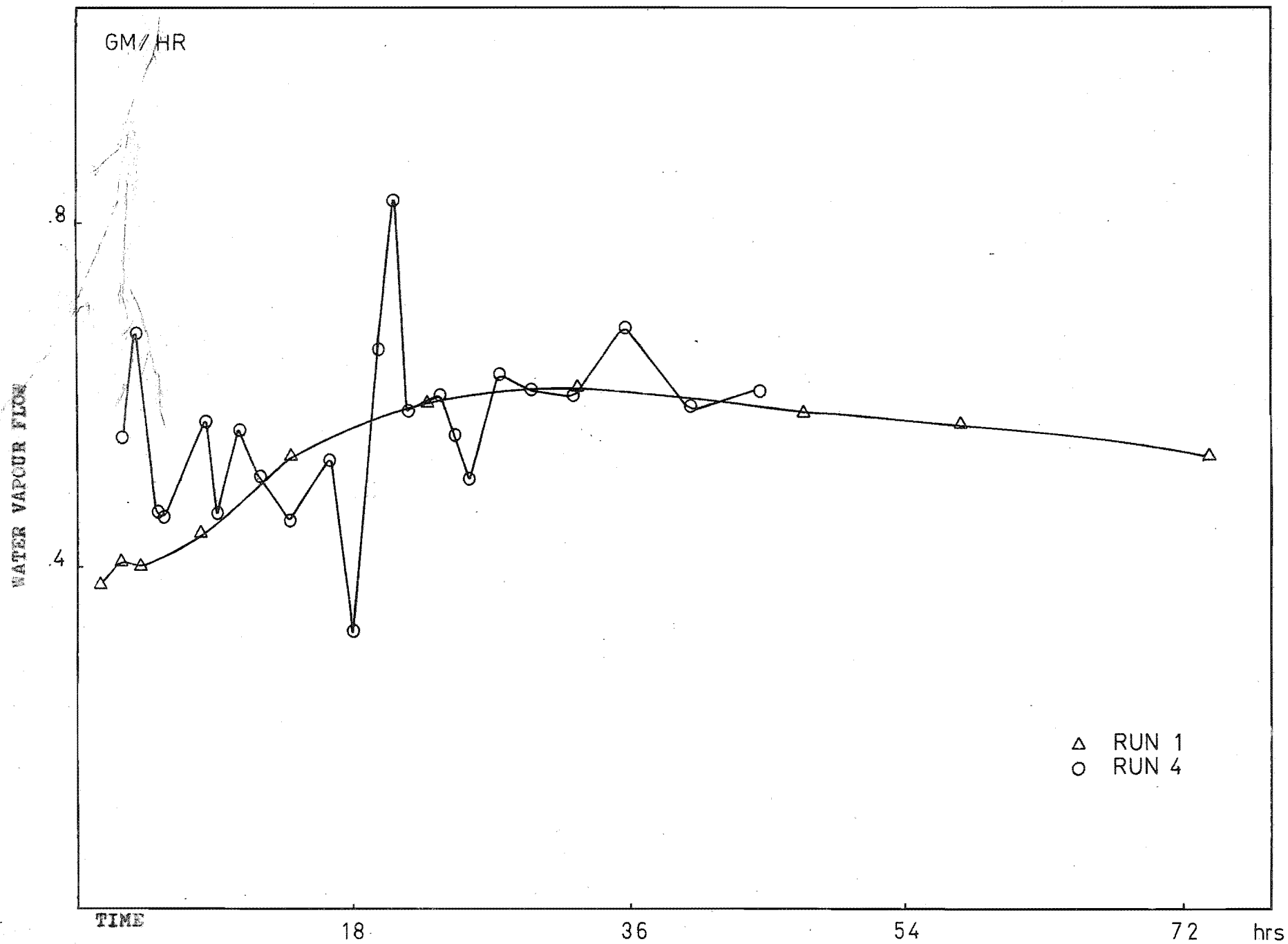


FIGURE 13. OUTLET WATER VAPOUR FLOW

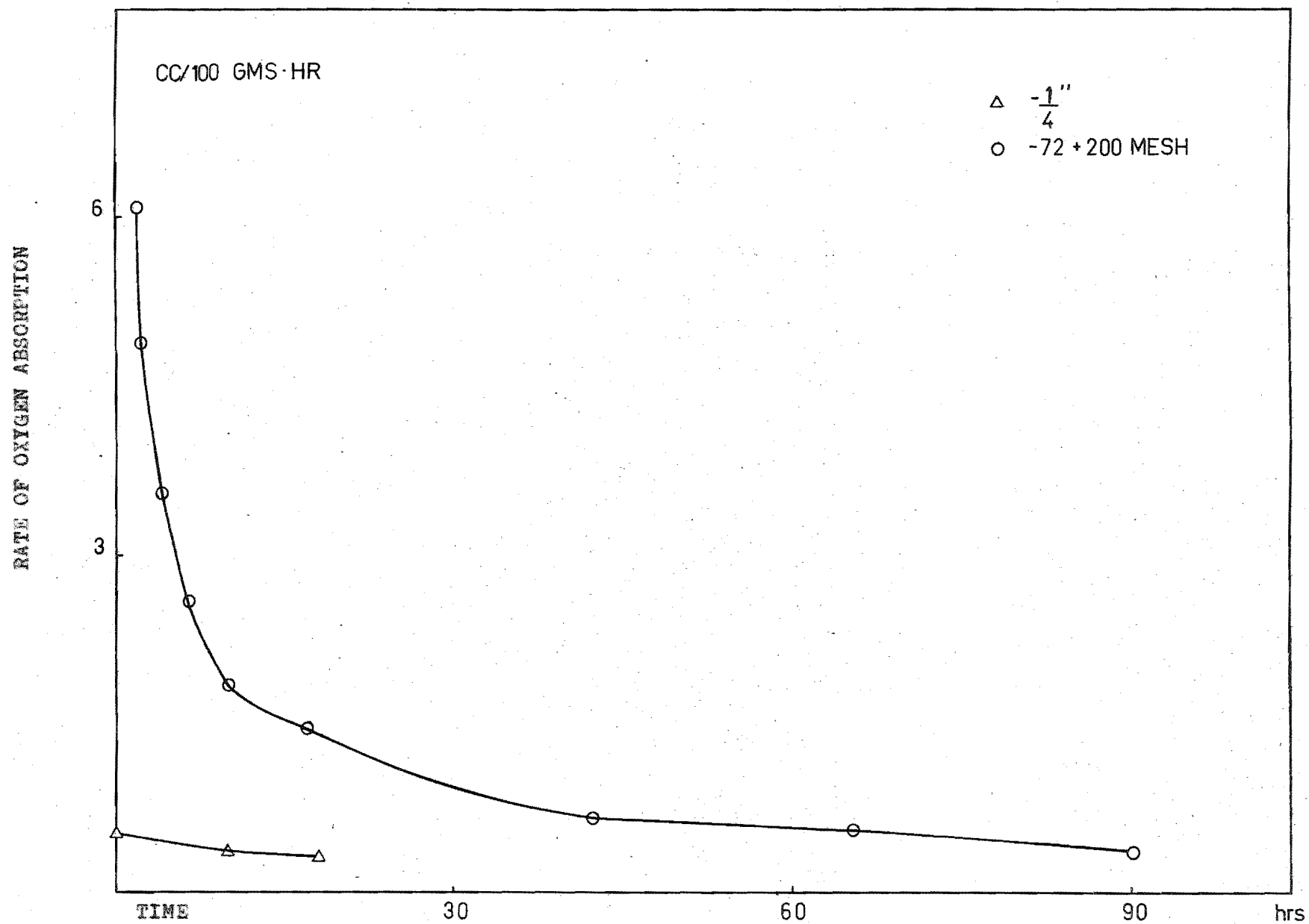


FIGURE 14. RATE OF OXYGEN ABSORPTION · 23 °C

## CHAPTER SIX

### PRELIMINARY COMPUTATIONS

#### Method of Computation

The method of solving the energy equation by finite difference formulae which had been used, was by forming the finite difference equation by using the values at two time levels, and the values of temperature rise, change in air, oxygen, carbon dioxide, coal oxidation and moisture content at each point, were iterated until they reached a final value. The variables, used to form the equation, were calculated at each iteration step. This iteration for each point was within another iteration for the convergence of the whole set of points along the path travelled by the air. The method was accurate because it did not involve many computation steps. However, it would be prohibitive if the problem was much more complex or the number of points to be solved was much larger.

The possibility of replacing the inner iteration of each point by solving the simultaneous finite difference equations of the whole set of points, could be verified only by actual computation.

It would be expected that the convergence of the outer iteration would be slower for this scheme. In the above-mentioned scheme, the iteration of each point was based on an already converged previous point, and an improved value of the next point, assuming convergence. The variables which formed the finite difference equation were calculated in each step, therefore they finally were calculated from a value which was more correct than it was initially.

The solutions obtained in one sweep through the points would, therefore, be closer to the final values than those obtained from the simultaneous equations. In fact, convergence was obtained, but only slowly, around 100°C.

Preliminary calculations showed that the method using the solution of the simultaneous equations was feasible, and the results were accurate.

#### Comparison of Low Temperature Oxidation Experiments and Calculations

The total absorption of oxygen in the column of coal was obtained from the outlet oxygen concentration and the flow rate of the gas. Gas analysis at each sampling point could not be carried out adequately to provide the rate of absorption of oxygen at each point, therefore the rate was assumed to be proportional to that evaluated by the rate equation, which had been used in previous computation.

Preliminary calculation showed that radial heat conduction should be taken into account, as the heat flow in this direction into the polystyrene was significant.

The calculation procedure is described in appendices 2 and 3 and the program is shown in Figure 50.

## CHAPTER SEVEN

### DISCUSSION

The experiments carried out consisted of low temperature oxidation experiments, to compare the accuracy of the equations describing the process of heating, and attempt to measure the heat of oxidation and the rates of oxidation of the coal used in the experiments. The computations were carried out for the low temperature oxidation experiments, using the equations which describe the process of heating. They were also carried out to assess the effects of diffusion of the gases in the voidage and the perfect gas law in the heating. The process of heating of a pile of coal was computed using a moisture content - vapour pressure relationship for the evaporation of moisture.

#### 1. Low Temperature Oxidation Experiments - Summary of Results

The evolution of carbon monoxide and carbon dioxide from one typical run are given in Table I. They correspond to the experiment whose results are shown in Figures 11, 12.

TABLE I - EVOLUTION OF CARBON MONOXIDE AND CARBON DIOXIDE  
IN RUN II

Hrs From Start	CO	CO <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	$\frac{CO}{O_2}$	$\frac{CO_2}{O_2}$
	percent	percent	percent	percent	percent	percent
5	0.009	0.26	12.5	87.24	0.093	2.38
15	0.007	0.29	14.8	84.9	0.097	4.03
29	0.0055	0.13	15.7	84.17	0.078	2.04
45	0.004	-	16.7	83.3	0.078	-
75	0.003	-	18.0	82.0	0.082	-

The ratios  $CO_2/O_2$  and  $CO/O_2$  are low in comparison with

those obtained from previous atmospheric oxidation of New Zealand sub-bituminous coal<sup>42</sup>. In the latter experiments the ratio increased as the heating developed and decreased as the temperatures fell.

Comparing them with the conditions usually found in mines, the above figures are similar to those found during the early stages of a heating.

Traces of methane were also found.

#### Rate of Oxidation Experiments

Rates of oxidation obtained for  $\frac{1}{4}$ " coal are shown in Figure 14. The rates were lower by a factor of 5 than those reported for the same New Zealand sub-bituminous coal previously<sup>88,89,42</sup>. It is suspected that the oxygen analyser which was being used for the first time may have been faulty.

#### Comparison of Experimental Results and those obtained from Computations

The computations were carried out from the initial data of run II shown in Figures 5, and 8. The ambient temperature was taken to be  $23 \pm 1^\circ\text{C}$ , and the rate of flow was  $4\text{cc}/\text{cm}^2 \text{ min} \pm 1\text{cc}/\text{cm}^2 \text{ min}$ .

The temperature rise in the column was initially computed from the total oxygen absorption obtained experimentally and no radial heat conduction was taken into account. The results are shown in Figure 15. They indicated that the heat loss into and through the polystyrene should be included in the computations, as the experimental temperatures shown in Figure 5 were much lower than those obtained by the computations, as the radial heat loss was considerable.

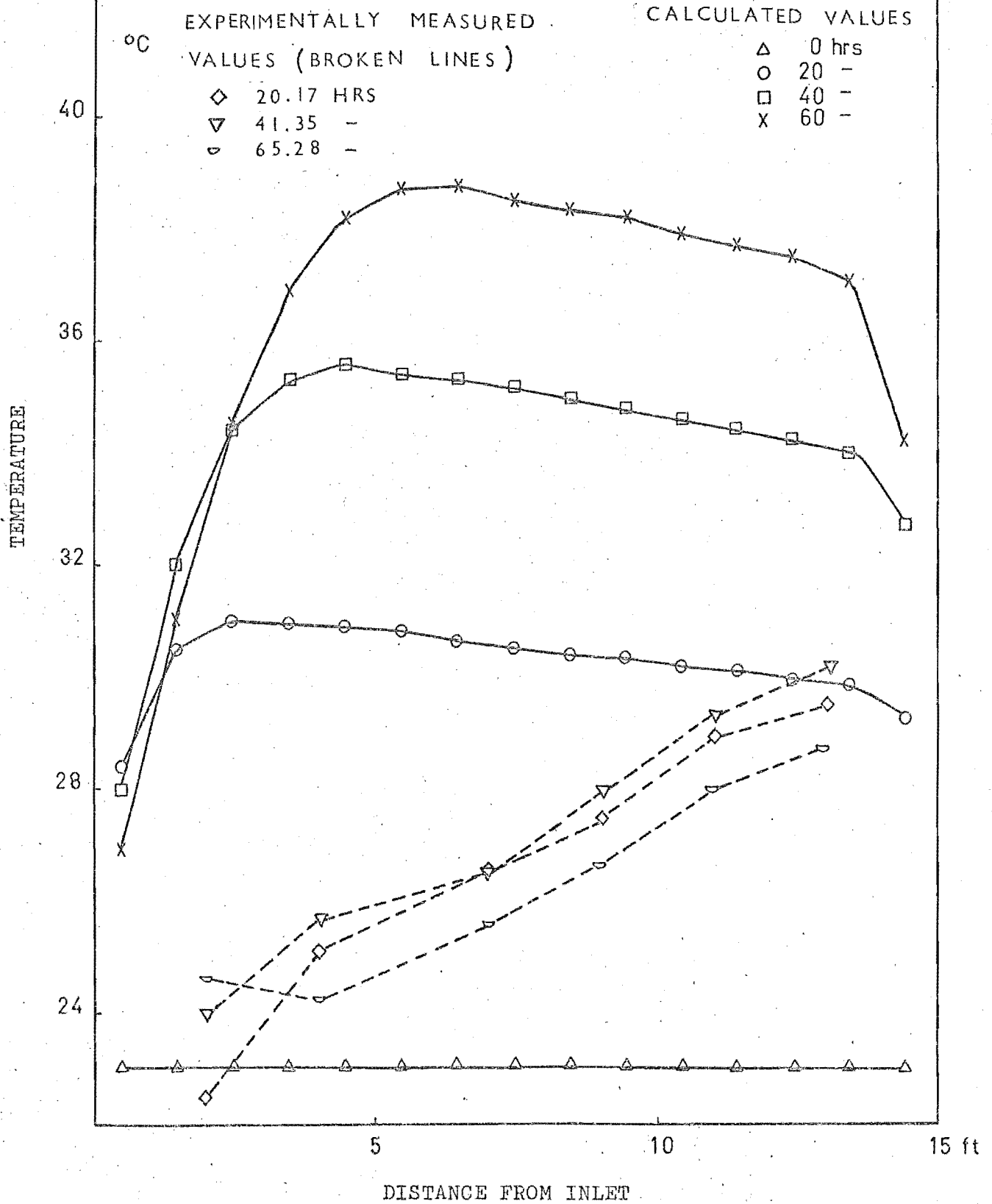


FIGURE 15 . TEMPERATURE HISTORY

CALCULATED FOR RUN 2 , PAGE 55

RATE OF FLOW 2CC/CM<sup>2</sup> MIN

NOT INCLUDING RADIAL HEAT CONDUCTION



The computations for the radial heat conduction are described in Appendix 2.

The computations for diffusion of the gases in the voids were also included, however it was shown in the one dimensional case of the process of heating in a pile of coal that the effect of diffusion, at the rate of flow used in the experiment, is negligible. Therefore the computations were carried out without the diffusion of the gases.

The program is described in Appendix 3.

Approximate heat balances are given in Table II to show the importance of the processes. They were obtained from the computations whose results are shown in Figures 21 to 25.

TABLE II - TYPICAL HEAT BALANCES

	1 ft from the inlet		14 ft from the inlet	
	12 hrs	30 hrs	12 hrs	30 hrs
	23.7°C	24.3°C	29.6°C	30.5°C
	Cal/1ft 6 hrs	Cal/1ft 6 hrs	Cal/1ft 6 hrs	Cal/1ft 6 hrs
Oxidation	+915	+605	+1954	+1262
Heat taken up by specific heat	-524	+ 30	- 722	+ 65
Axial conduc- tion	- 34	- 30	- 12	- 19
Convection	-1.5	-2.0	-	-
Radial Cond- uction	- 80	-281	-1046	-1161
Heat of wetting	-233	-319	- 43	- 35

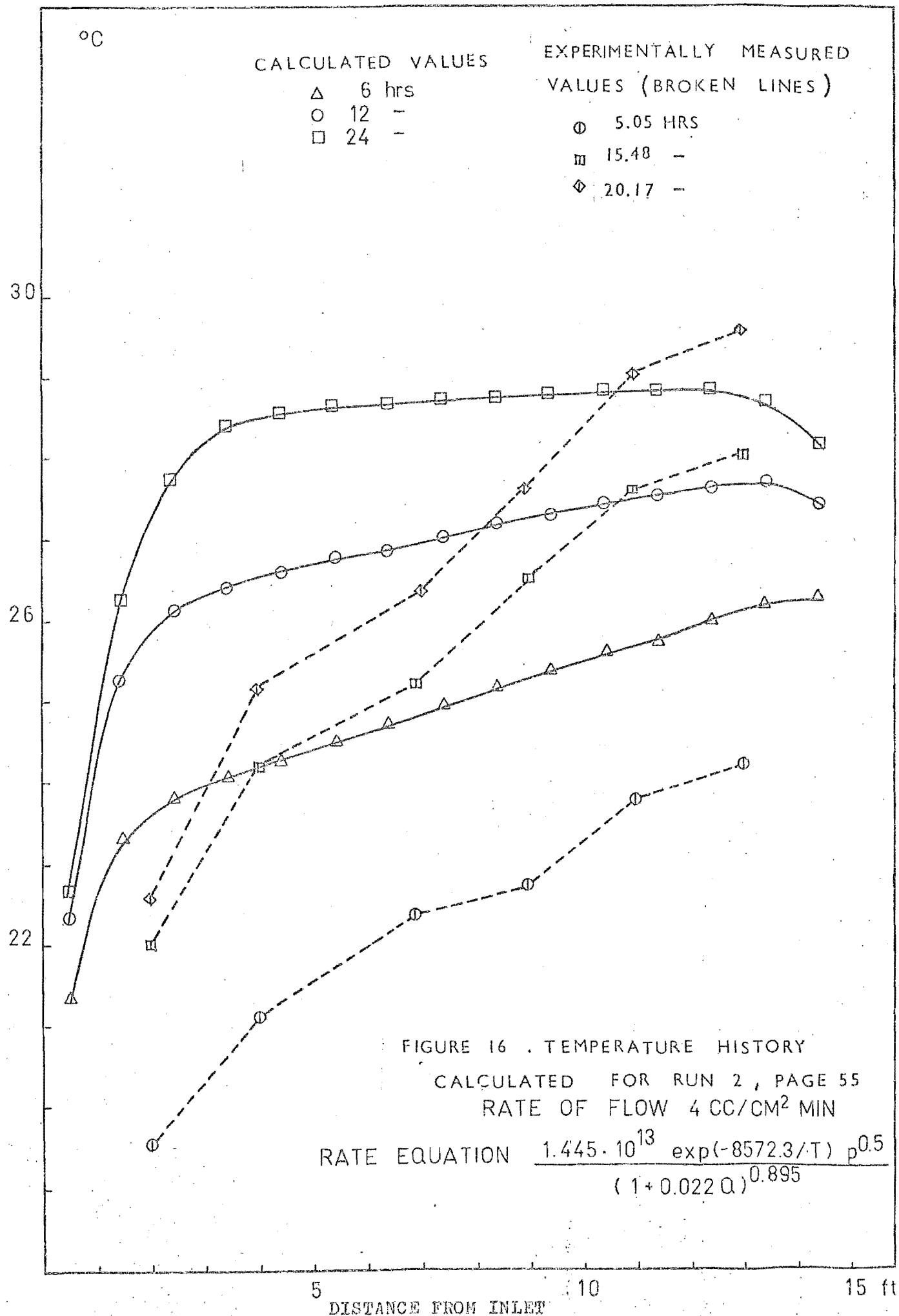
The heat of wetting was still not very important as the temperatures were low, however, it can be seen that the highest heat loss at the inlet region was by evaporation. The temperature at the inlet region was partly kept at values lower than that of other regions because of its higher rate of evaporation.

At the region having the highest temperature, nearly all the heat generated by oxidation was lost by radial heat conduction in the late stages of the experiment.

In the initial computations, the rate of oxidation which has been used in previous calculations, was used, i.e. the coal was assumed to have an activation energy of 17 Kcal/mole, the order of reaction of the oxygen with the coal was 0.5.

The results obtained are shown in Figure 16. They clearly indicate that the coal used in the experiment was more reactive than the assumed rates used in the computations, because the temperature at the hotter region, i.e. at the outlet end, increased much faster than the rate of increase in temperature as shown by the computed results.

Possible causes of these differences are discussed below. They include fluctuations in ambient temperature, rate of flow, and by factors pertaining to the oxidation of the coal: order of reaction, temperature dependent coefficient, decrease in the rate of oxidation with the extent of oxidation and the heat of oxidation per unit volume of oxygen absorbed.



### Ambient Temperature and Rate of Flow

The ambient temperature could be controlled within  $\pm 1^{\circ}\text{C}$ . The rate of flow was found to fluctuate within  $\pm 25$  percent of its average value.

Figure 27 shows the temperature curves calculated for a rate of flow at  $4 \text{ cc/cm}^2 \text{ min}$ , and Figure 28 shows the temperature curves calculated for a rate of flow at  $3 \text{ cc/cm}^2 \text{ min}$ , which are equivalent to those for the rate of flow at  $4 \text{ cc/cm}^2 \text{ min}$  using a value of the heat of oxidation of  $2.25 \text{ cal/cc}$  of oxygen absorbed. From the experimental temperature curves shown on Figure 5, the results of a rate of flow of  $4 \text{ cc/cm}^2 \text{ min}$  are more similar to the experimental results than those at  $3 \text{ cc/cm}^2 \text{ min}$ . Therefore the value of the rate of flow of  $4 \text{ cc/cm}^2 \text{ min}$  and the heat of oxidation of  $3 \text{ cal/cm}^2 \text{ min}$  appear to correctly describe the oxidation of coal, and these values correspond to those used in the experiment with experimental errors.

We would not expect the fluctuations in the ambient temperature and the rate of flow to have an appreciable effect in the experiment. The ambient temperature varies periodically within  $\pm 1^{\circ}\text{C}$ , therefore its effect is not long lasting.

The rate of flow has a considerable effect at the initial stage of the oxidation when the rate of absorption of the oxygen is so high that the outlet oxygen concentration is greatly reduced. However, this initial stage is quickly passed. From Figure 8, it can be seen that the outlet oxygen concentration is approximately 15 percent. If the order of reaction

TEMPERATURE

CALCULATED VALUES

- $\Delta$  6 hrs  
 $\circ$  12 -  
 $\square$  18 -  
 $\times$  24 -

EXPERIMENTALLY MEASURED  
VALUES (BROKEN LINES)

- $\oplus$  5.05 HRS  
 $\boxplus$  15.48 -  
 $\diamond$  20.17 -

 $^{\circ}\text{C}$ 

30

26

22

FIGURE 17 . TEMPERATURE HISTORY

CALCULATED FOR RUN 2, PAGE 55  
 RATE OF FLOW 4 CC/CM<sup>2</sup>MIN

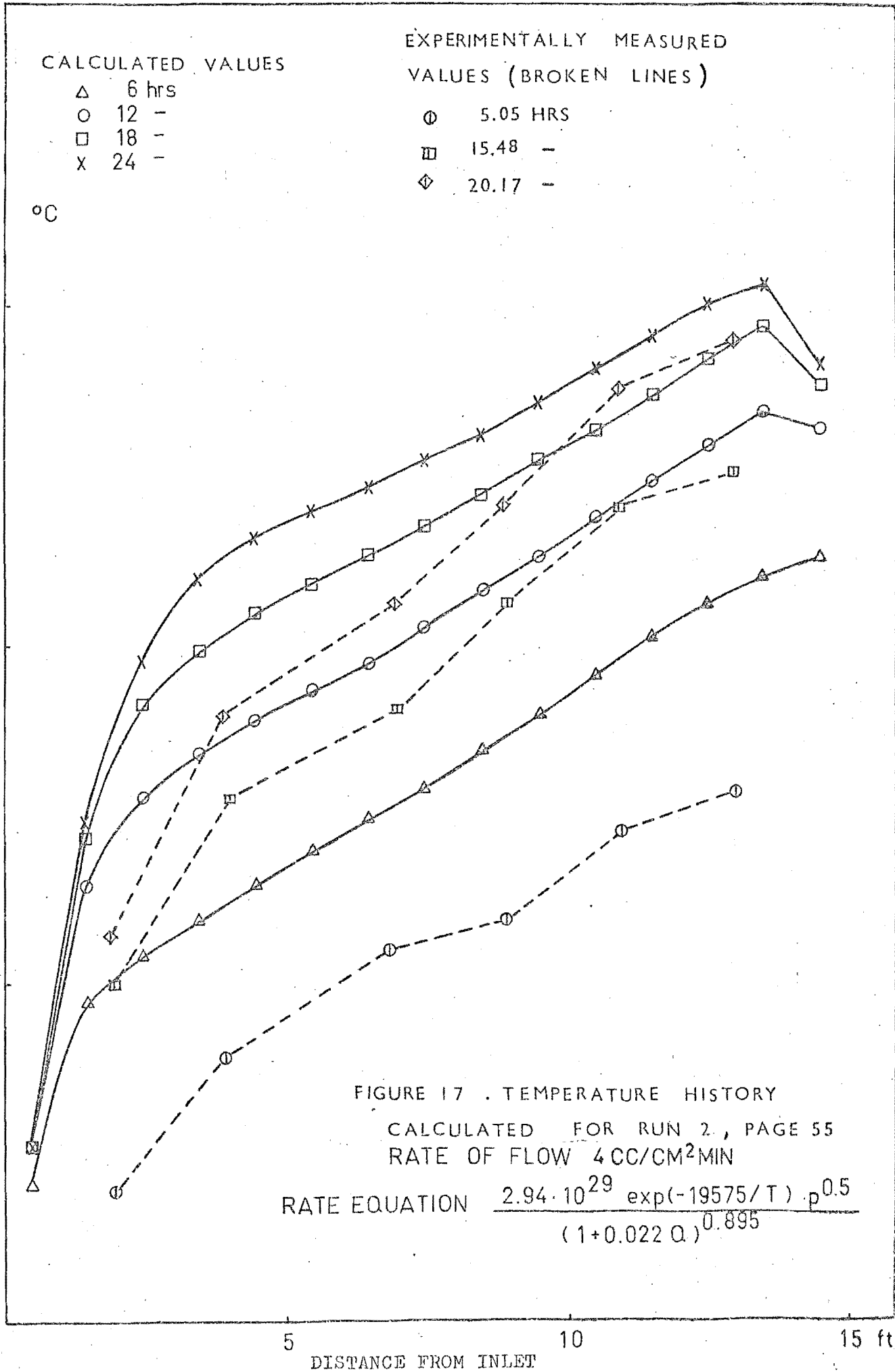
RATE EQUATION  $\frac{2.94 \cdot 10^{29} \exp(-19575/T) \cdot p^{0.5}}{(1+0.022 Q)^{0.895}}$

5

10

15 ft

DISTANCE FROM INLET



°C

CALCULATED VALUES

$\Delta$  6 hrs  
 $\circ$  12 -  
 $\square$  24 -

EXPERIMENTALLY MEASURED  
VALUES (BROKEN LINES)

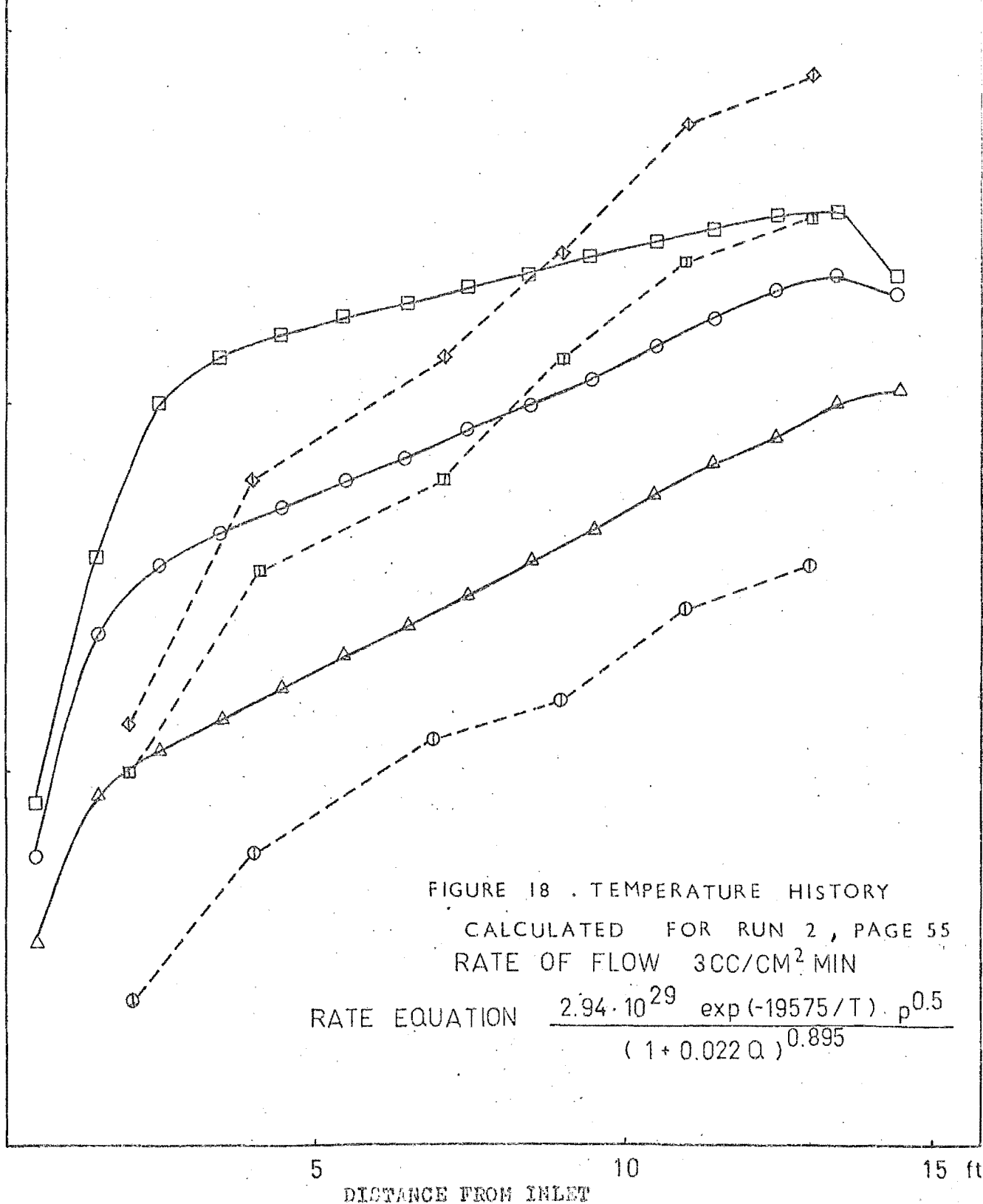
$\oplus$  5.05 HRS  
 $\boxplus$  15.48 -  
 $\diamond$  20.17 -

30

26

22

TEMPERATURE



is 0.5 changing the concentration in the air from 15 percent to 17 percent of oxygen, changes the rate of oxidation by a factor of 1.06 only. This is small considering errors caused by other factors. Therefore if a rate of flow of  $4 \text{ cc/cm}^2\text{min}$  gives an outlet oxygen concentration of 15 percent, a rate of flow of  $6 \text{ cc/cm}^2\text{min}$  will give an outlet oxygen concentration of 17 percent, and the effect of a change of flow on the rate of oxidation is therefore negligible. Therefore a change in rate of flow from  $4 \text{ cc/cm}^2\text{min}$  to  $6 \text{ cc/cm}^2\text{min}$  would be shown as a change from 15 percent to 17 percent in the outlet oxygen concentration. It can be seen that there are no fluctuations of this extent on the experimental outlet oxygen concentration curves shown in Figure 8.

Therefore the effects of the external conditions in the experiment are negligible. The accuracy of the results from the experiment is not affected appreciably by fluctuations in the experimental conditions, therefore the experiment provides accurate results on the oxidation of coal.

#### Effect of Temperature-Dependent Coefficient in the Equations

If the data on the rates of oxidation of -72 + 200 mesh New Zealand sub-bituminous coal, obtained by Stott<sup>92</sup> for the temperature range from  $20^\circ\text{C}$  to  $46^\circ\text{C}$ , are used to obtain the activation energy of the oxidation, a value of the order of 39 Kcal/mole is obtained. This value is approximately constant for different degrees of oxidation, from an absorption of 100 cc of oxygen/100 gm of coal to 500 cc of oxygen/100 gm of coal.



This value is high, however, it is not impossible that the value of the activation energy may be different at higher ranges of temperatures, as the mechanism of the absorption of oxygen changes and therefore the activation energy is changed, as one investigator<sup>82</sup> has found.

The activation energy has been found to change with the extent of oxidation only during the first few minutes of the oxidation. The rates of oxidation obtained by Winmill<sup>102</sup>, Graham<sup>33</sup>, Schmidt and Elder<sup>78</sup>, show constant values of activation energy, when the extent of oxidation has passed the initial stages.

From the states of oxidation obtained by Winmill<sup>107</sup>, from coals of size -2 + 10 mesh and -200 mesh we obtain the same activation energy. The same result has been observed by other investigators<sup>8</sup>.

Figure 16 shows the temperature curves obtained for a value of activation energy of 17 Kcal/mole, Figure 17 shows the temperature curves obtained for an activation energy of 39 Kcal/mole. The order of reaction is 0.5.

It can be seen that the results obtained for an activation energy of 39 Kcal/mole are more similar to the experimental results in Figure 5, than the results obtained with an activation energy of 17 Kcal/mole.

#### Effect of the Order of Reaction

The order of reaction of the coal-oxygen reaction has been found to have values from 0.5 to 0.61<sup>107,78</sup>. It is

noted that the value of 0.61 found by Schmidt and Elder<sup>78</sup> was from the rates of oxidation of the same sample of coal as it was being oxidised in an atmosphere where the oxygen concentration was continuously decreased. Therefore, an additional factor caused by the decrease of the rate of oxidation with the extent of oxidation was introduced, and the order of reaction was therefore less than 0.61.

Figure 21 shows the temperature curves obtained for an order of reaction of 0.4. Figure 17 shows the temperature curves obtained for a value of 0.5, and Figure 19 shows those obtained for a value of 0.7.

From the experimental temperature curves shown on Figure 5, it can be seen that the values of 0.4 and 0.5 give temperature curves which are similar to the experimental curves. However, the difference between the value of 0.4 and 0.5 is too small to allow a correct evaluation of the order of reaction.

The order of reaction has a smaller effect than other factors in the rates of oxidation in the experiments, because the oxygen concentration was not reduced to a great extent during most of the oxidation process.

#### Effect of the Decrease of the Rate of Oxidation with the Extent of Oxidation

The rates of oxidation obtained by Graham for - 200 mesh coal at temperatures from 30°C to 160°C show that the decrease in the rate of oxidation is proportional to a constant power of the extent of oxidation. The value of the power is 1.5. However, the rates of oxidation of - 2 + 10 mesh coal obtained

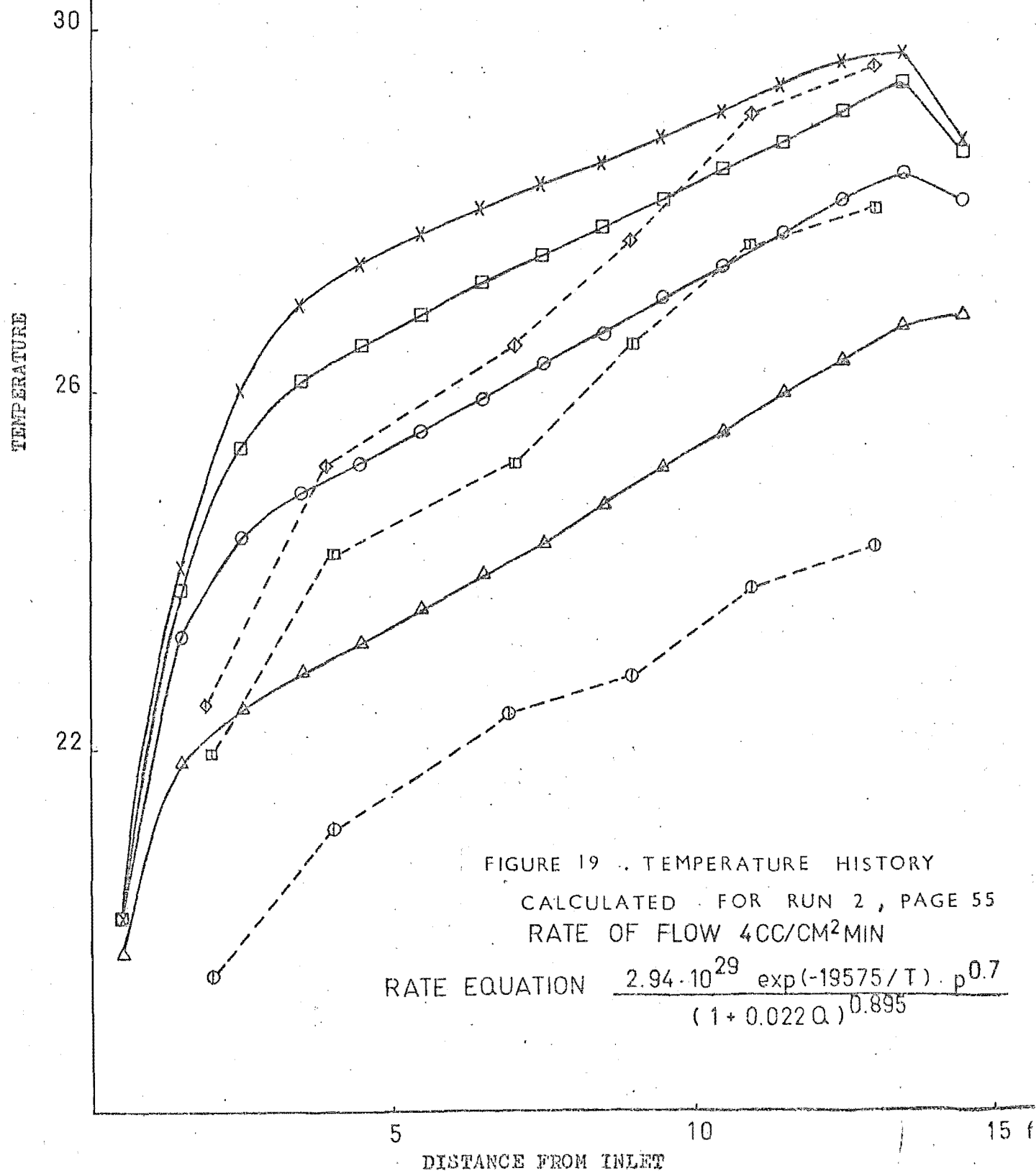
°C

CALCULATED VALUES

$\Delta$  6 hrs  
 $\circ$  12 -  
 $\square$  18 -  
 $\times$  24 -

EXPERIMENTALLY MEASURED  
VALUES (BROKEN LINES)

$\odot$  5.05 HRS  
 $\square$  15.48 -  
 $\diamond$  20.17 -



by Winmill<sup>107</sup> at 30°C and 50°C show that the decrease in the rate is not proportional to just one power of the extent of oxidation for different values of the extent of oxidation. In these results, when the extent of oxidation varied from 100 cc of O<sub>2</sub> absorbed/100 gm of coal to 300 cc of oxygen absorbed/100 gm of coal, the rates can be correlated to those of -200 mesh coal by a constant factor, which Schmidt<sup>77</sup> obtained as the cube root of the external surface area. The decrease in the rate of oxidation of -2 + 10 mesh coal in this range of extent of oxidation is therefore also proportional to the power 1.5 of the extent of oxidation. When the extent of oxidation is less than 100 cc of oxygen/100 gm of coal, the decrease in the rate of oxidation is proportional to the power 0.2 of the extent of oxidation, which shows that the change in the rates of oxidation of coarse coal is much slower than that of fine coal during the initial stages, which is probably due to a different mechanism in the initial stages of the coal - oxygen absorption.

The decrease in the rate of oxidation obtained for New Zealand sub-bituminous coal from the rates obtained for -72 + 200 mesh<sup>92</sup> was found to be proportional to a power of 0.9 of the extent of oxidation. This power had been used in previous calculations by Murtagh<sup>71</sup>. For the coal used in the experiment, the decrease in the rate of oxidation with the extent of oxidation is different from that of a single size of coal, because there are different sizes and the fine size coals are oxidised to a greater extent than the coarser coals during the oxidation process. It can be expected that initially the rate of oxidation is contributed to mainly by

the fine coal, therefore the decrease in the overall rate is similar to the decrease in the rate for fine coal. However, the rate of oxidation of fine coal decreases much more quickly with time, as it absorbs more oxygen than the coarse coal, therefore, eventually the rate of the coarse coal is the main term in the overall rate and therefore the decrease in the overall rate is similar to that of the coarse coal. From the size distribution of the coal used in the experiment, there is fifty percent of coal in sizes larger than  $\frac{1}{10}$ ", therefore, the rate of the coarse coal becomes dominant quickly.

Figure 21 shows the computed temperature curves. Figure 5 shows the experimental temperature curves. It can be seen that the region which has the highest temperature shows a decrease in temperature after 36 hours, by the computed results, while the experimental results show that the temperature at this region was still increasing and reached the maximum value at 41 hours.

It has been shown that the experimental conditions have a negligible effect on the oxidation process. It is highly unlikely that the activation energy can be higher than 39 Kcal/mole, or the order of reaction can be much smaller than 0.4. Also, these factors have an effect in the earlier stages of the oxidation. Therefore the difference in the computed results and the experimental results is most probably caused by the difference in the decrease of the rate of oxidation of the coal used in the experiment and that used in the computations.

Figure 20 shows the temperature curves obtained when the decrease in the rate of oxidation is proportional to the power 0.27 of the extent of oxidation. The results show that the maximum temperature computed after 18 hours is approximately 3°C higher than that observed in the experiment, therefore, the decrease in the rate of oxidation is quicker than to the power 0.27 of the extent of oxidation.

The above discussions show the effects of the factors in the rate of oxidation on the heating in the column. The results obtained with values which were obtained by previous investigators, show that these factors change the results considerably. Obviously, the correct values of these factors can only be found by systematic studies of the kinetics of oxidation of the coal.

The most significant fact is that with the correct expression for the rates of oxidation, the processes which have been used to describe the process of heating of coal, describes the oxidation of coal in the column accurately.

The results also show the complexity of the oxidation of coal. The computations have shown that the two important processes in the heating are the oxidation and the evaporation of moisture. It can be seen that these processes are greatly influenced by parameters such as size and temperature. Therefore, difficulties arise when the theoretical considerations are used to predict the liability of piles of coal in mines to fire.

Errors can also arise when the rates of oxidation used in the computations of the process of heating are obtained

EXPERIMENTALLY MEASURED

CALCULATED VALUES

°C

VALUES (BROKEN LINES)

⊕ 5.05 HRS

△ 6 hrs

⊠ 15.48 -

○ 12 -

⬠ 20.17 -

□ 18 -

30

26

22

FIGURE 20 . TEMPERATURE HISTORY

CALCULATED FOR RUN 2 , PAGE 55

RATE OF FLOW 4CC/CM<sup>2</sup>MIN

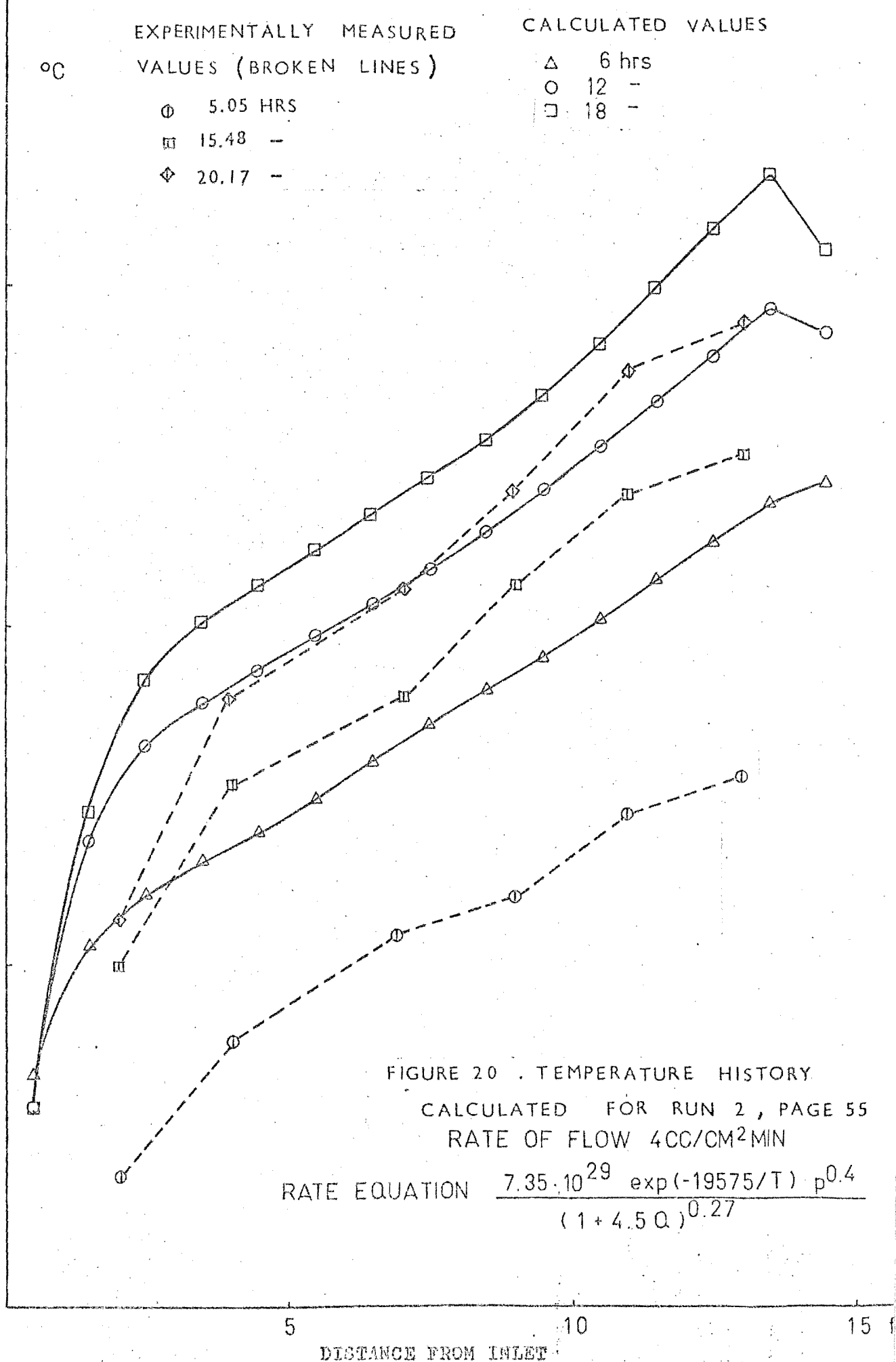
$$\text{RATE EQUATION } \frac{7.35 \cdot 10^{29} \exp(-19575/T) p^{0.4}}{(1 + 4.5 Q)^{0.27}}$$

5

10

15 f

DISTANCE FROM INLET



EXPERIMENTALLY MEASURED

CALCULATED VALUES

°C

VALUES (BROKEN LINES)

① 5.05 HRS

□ 15.48 -

◇ 20.17 -

⊖ 29.32 -

▽ 41.35 -

△ 45.50 -

⊕ 65.28 -

△ 6 hrs

○ 12 -

□ 18 -

◇ 24 -

⊖ 30 -

▽ 36 -

⊖ 42 -

⊖ 48 -

⊖ 54 -

30

26

22

FIGURE 21 . TEMPERATURE HISTORY

CALCULATED FOR RUN 2 , PAGE 55

RATE OF FLOW 4 CC/CM<sup>2</sup>MIN

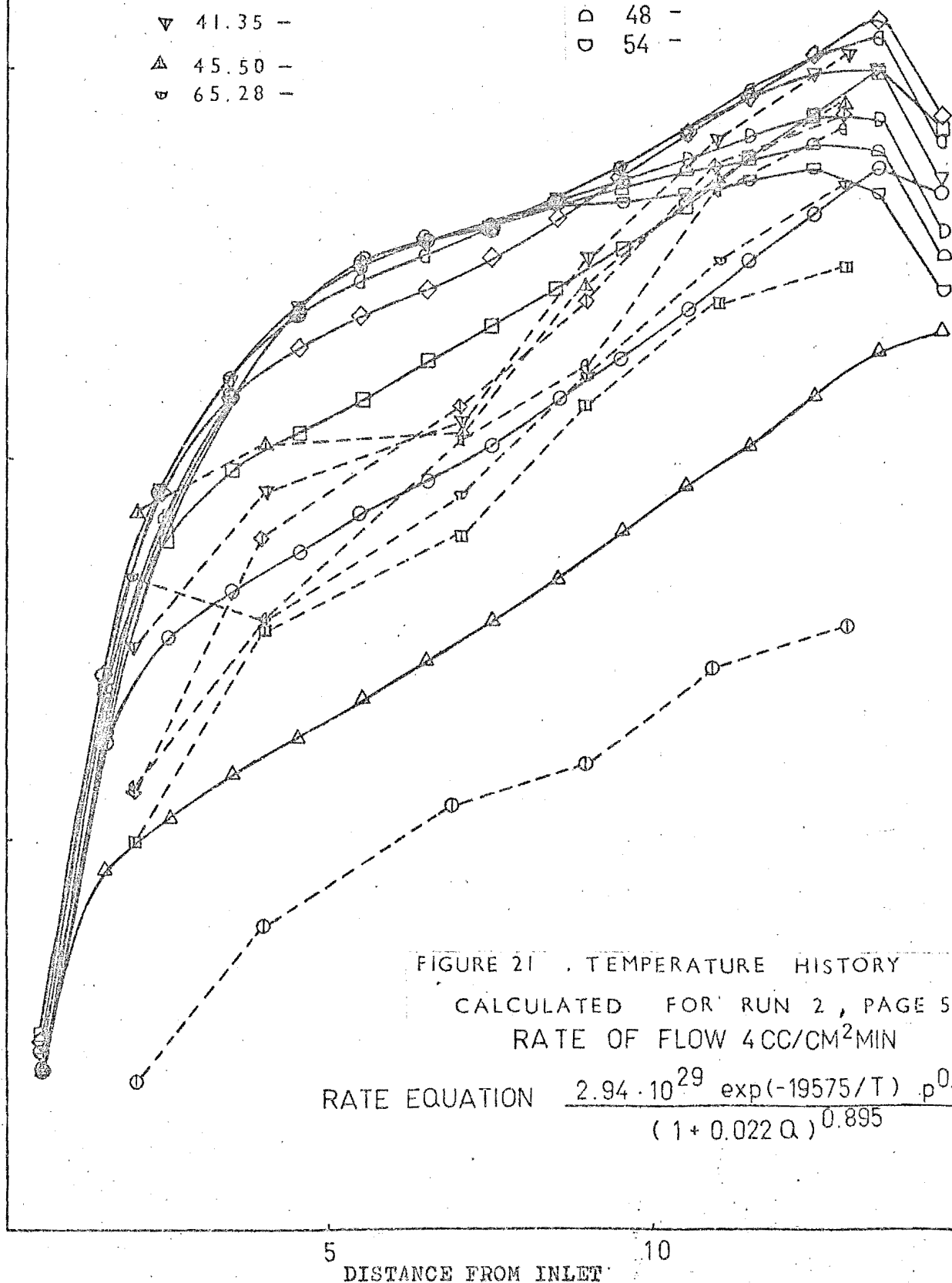
RATE EQUATION  $\frac{2.94 \cdot 10^{29} \exp(-19575/T) p^{0.4}}{(1 + 0.022 Q)^{0.895}}$

5

DISTANCE FROM INLET

10

15 ft





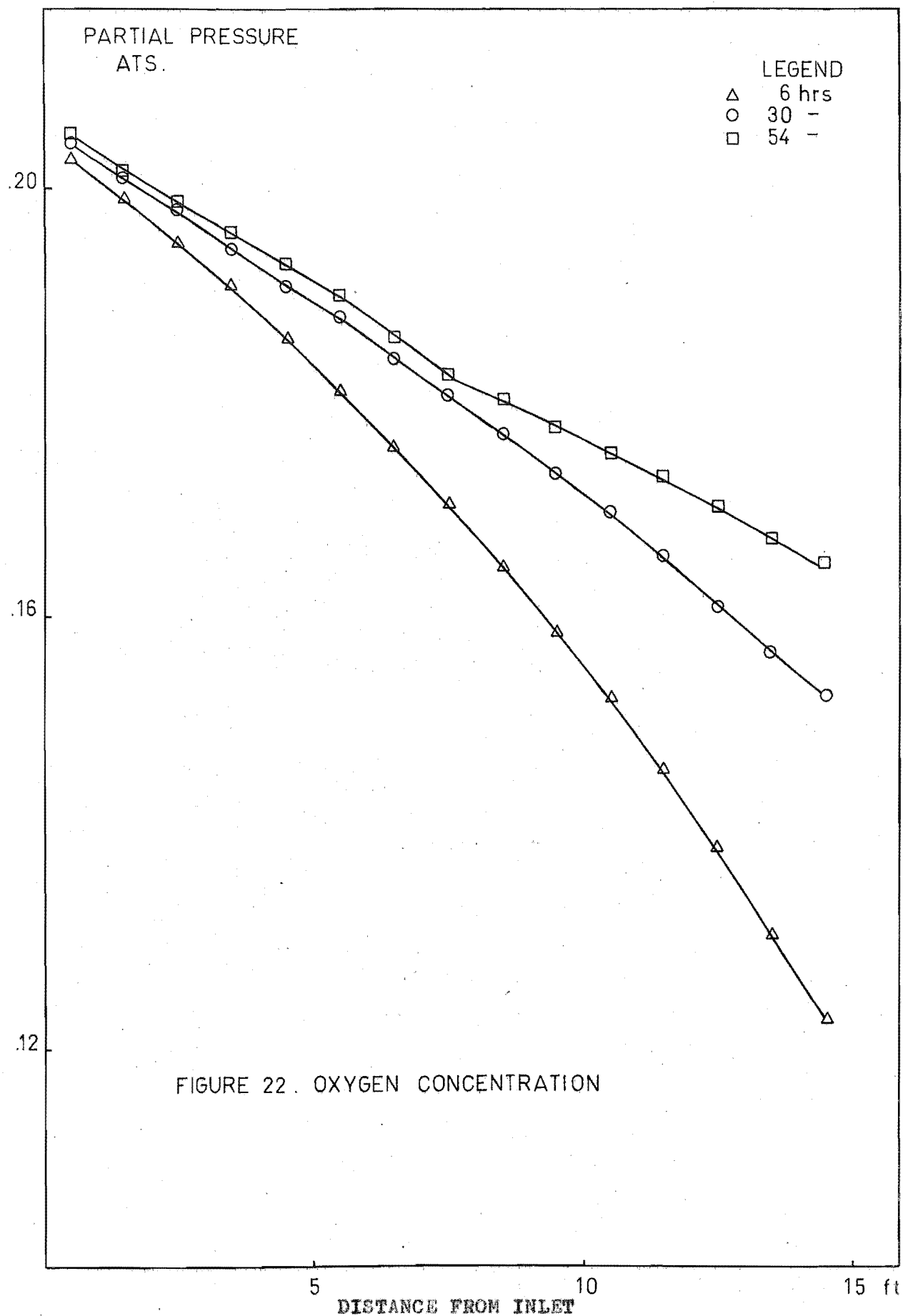
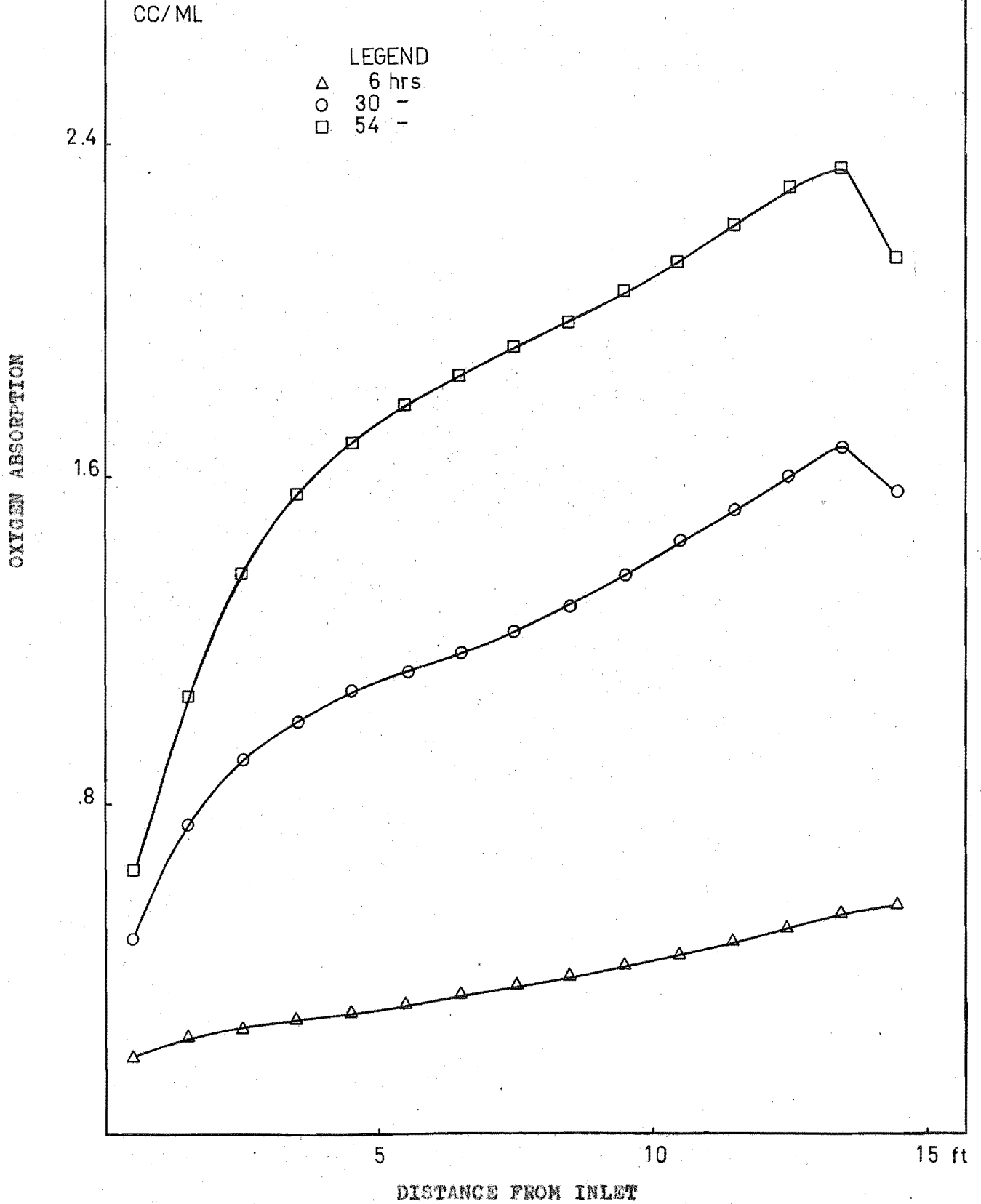


FIGURE 23. OXYGEN ABSORPTION



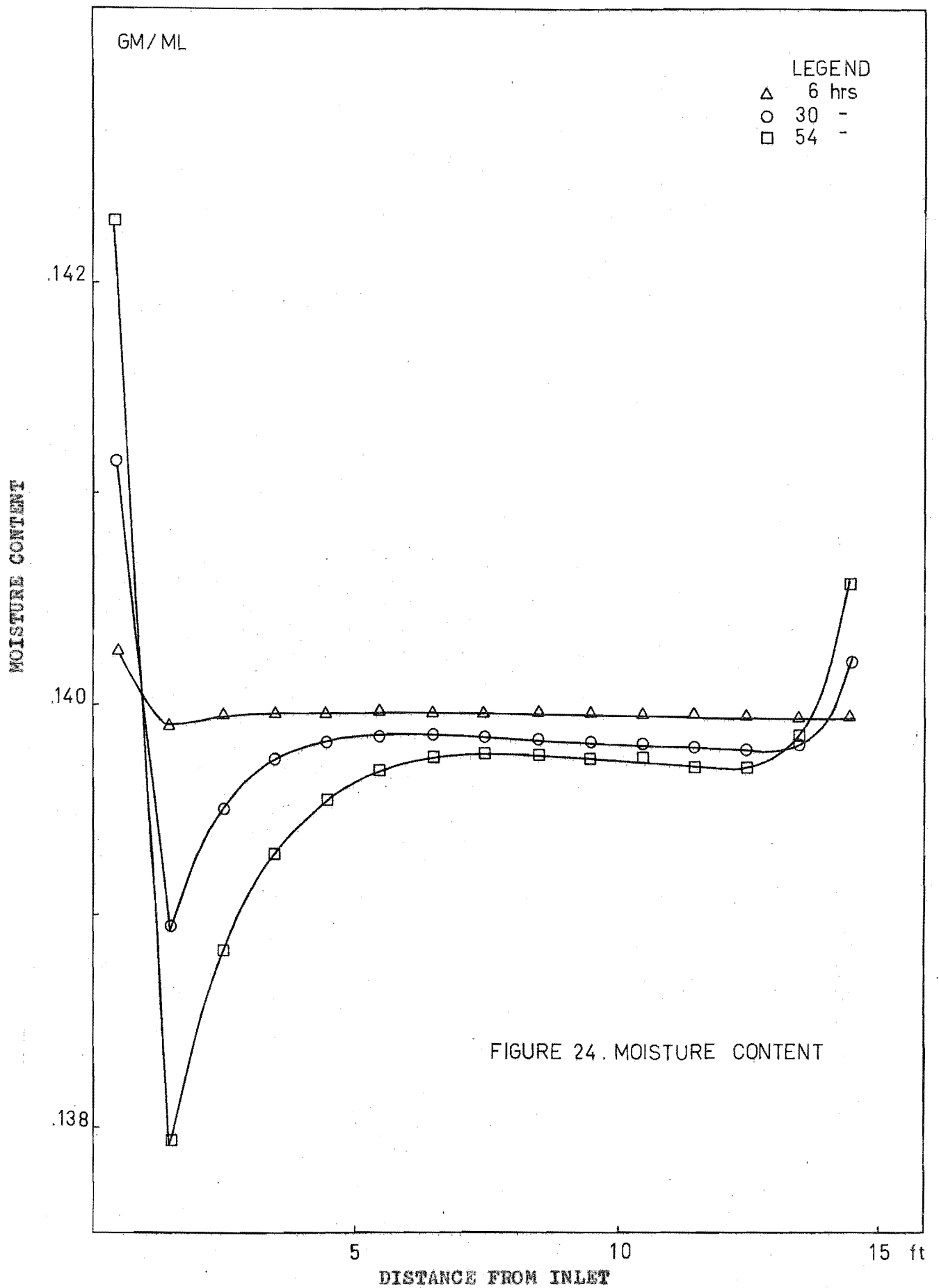
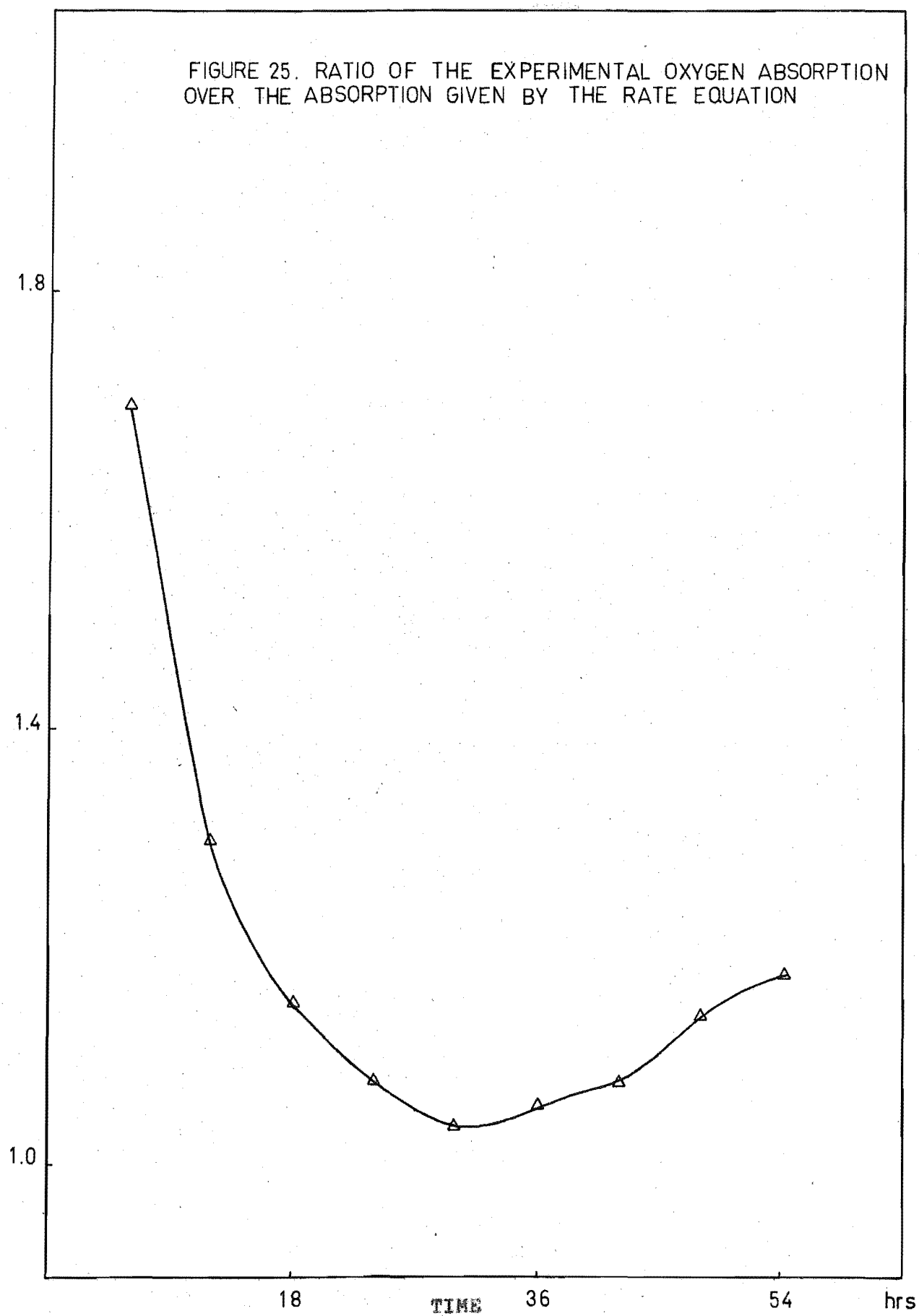


FIGURE 25. RATIO OF THE EXPERIMENTAL OXYGEN ABSORPTION  
OVER THE ABSORPTION GIVEN BY THE RATE EQUATION



from isothermal experiments. That is, is it legitimate to assume that at a given temperature, a coal which has actually absorbed a given quantity of oxygen will always oxidise at the same rate regardless of its previous oxidation history? In view of the complexity of the oxidation process, the assumption needs to be proved, and as far as the author is aware, this has not been done.

However, the calculated results do agree with experimental results with sufficient accuracy to indicate that the mechanism of spontaneous heating is sufficiently described by the equations used.

## 2. The Significance of results from the Simulation

The program which simulates the process of heating in a pile of coal, i.e. by solving the one dimensional energy and continuity equation, using the vapour pressure - moisture content relationship, is described in Appendix 4.

The rates of oxidation which had been used for previous calculations are used in the computations. The results obtained by using these rates of oxidation are still significant if they are less than those of New Zealand sub-bituminous coal in the size range -2 + 10 mesh.

The vapour pressure - moisture content relationship used in the computations are shown in Figure 26. They were derived from data obtained by Kreulen<sup>64</sup>. The shape of the curves was fitted to the moisture content range of sub-bituminous coal (see Table III).

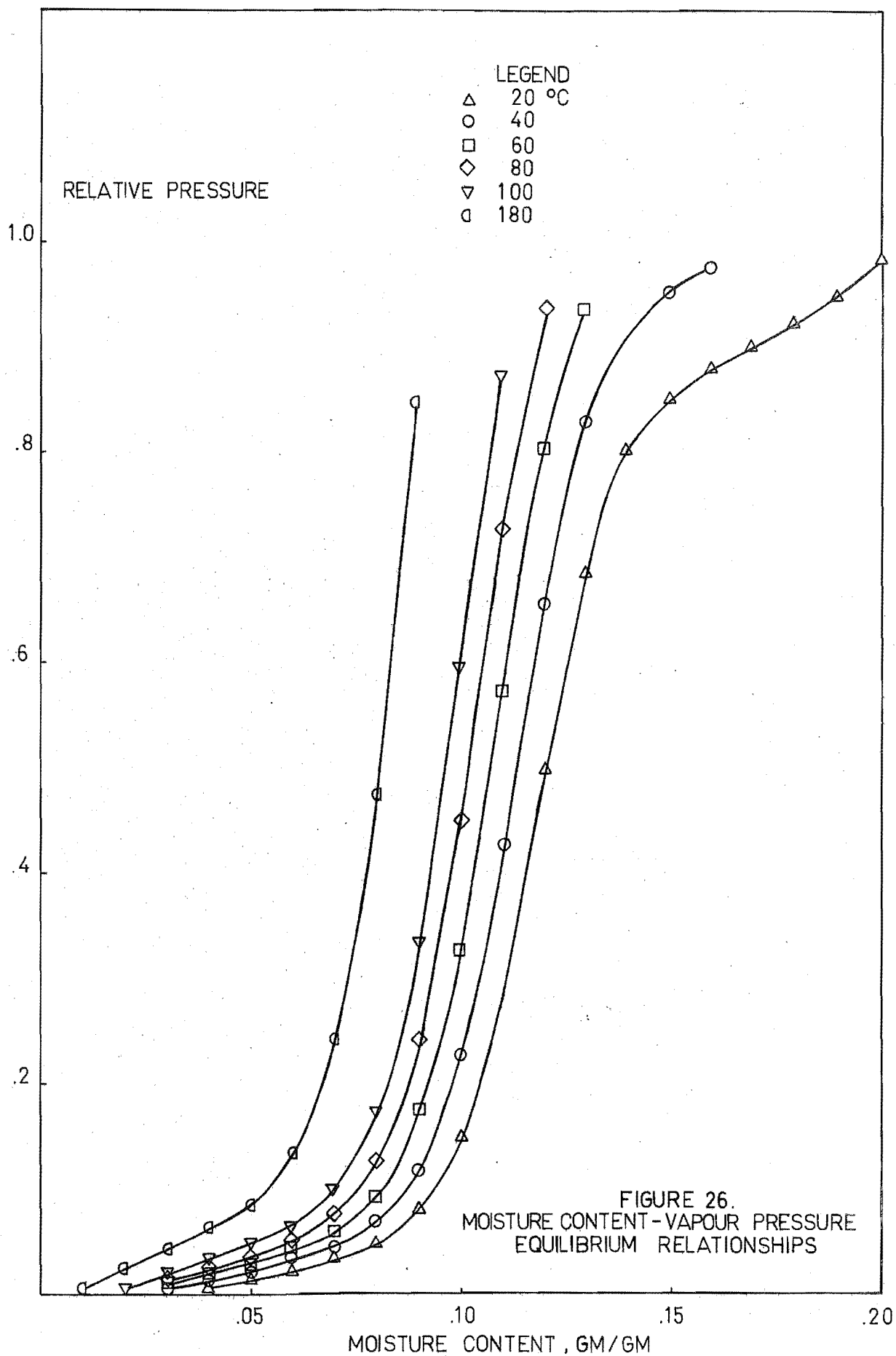


FIGURE 27. DRYING-RATE CURVES (WILSON<sup>121</sup>)

LEGEND	PARTICLE SIZE	TEMPERATURE	GAS VELOCITY
△	$\frac{1}{4}$ - $\frac{1}{8}$	80 °C	.35 CM/MIN
○	-8 +16 MESH	80 -	.36 -
□	$\frac{1}{32}$ - $\frac{1}{64}$	80 -	.44 -
◇	$\frac{1}{4}$ - $\frac{1}{8}$	95 -	.75 -
▽	-8 +16 MESH	98.5 -	.66 -
◊	$\frac{1}{32}$ - $\frac{1}{64}$	95 -	.77 -

LENGTH OF BED 1 PARTICLE LAYER

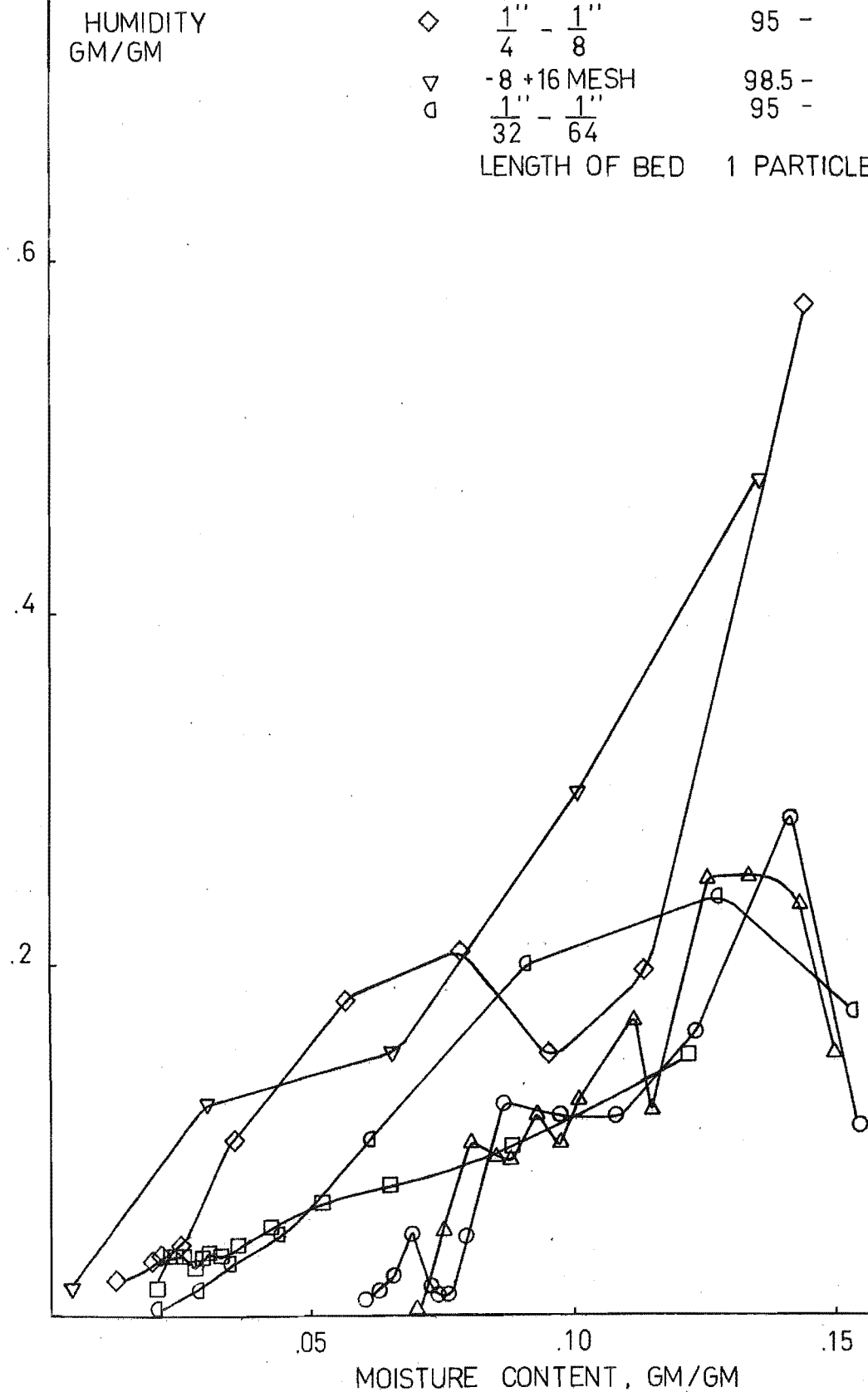


TABLE III - EXPRESSIONS USED IN THE CALCULATIONS

Rate equations

$$\begin{aligned}
 \text{(i)} \quad \frac{dO}{dt} &= \frac{2.94 \cdot 10^{29} \exp(-19575/T)}{(1 + 0.022Q)^{0.895}} \left(\frac{p}{p_o}\right)^{0.5} \\
 \text{(ii)} \quad \frac{dO}{dt} &= \frac{2.94 \cdot 10^{29} \exp(-19575/T)}{(1 + 0.022Q)^{0.895}} \left(\frac{p}{p_o}\right)^{0.7} \\
 \text{(iii)} \quad \frac{dO}{dt} &= \frac{2.94 \cdot 10^{29} \exp(-19575/T)}{(1 + 0.022Q)^{0.895}} \left(\frac{p}{p_o}\right)^{0.4} \\
 \text{(iv)} \quad \frac{dO}{dt} &= \frac{7.35 \cdot 10^{29} \exp(-19575/T)}{(1 + 4.5Q)^{0.27}} \left(\frac{p}{p_o}\right)^{0.4}
 \end{aligned}$$

Equations (i), (ii) and (iii) were used in the determination of the order of reaction. Equations (iii) and (iv) were used in the determination of the decrease of the rate of reaction with the extent of oxidation.

Moisture content - vapour pressure relationships:

(i) Saturation vapour pressure:

$$x = 0.025T - 8.325$$

$$p_o = (169.0655392047897 + 169.3123406453609$$

$$T_o(x) + 30.02063943390651 T_1(x)) / (1 -$$

$$0.5849736032823395 T_o(x) + 0.0700755257691317 T_1(x))$$

(ii) Bound moisture content:

$$x = 0.008695652173913042T - 3.547826086956521$$

$$W_o = (0.0114073759463767 - 0.01155729906766941$$

$$T_o(x)) / (1 + 0.3155538086932042 T_o(x))$$

(iii) Moisture content - vapour pressure relationship at 20°C:

$$W_1 = W - W_o$$

$$x = 11.90476190476194 W_1 - 1$$

$$p = ((0.4036771495265499 + 0.633288427578647$$

$$T_o(x) + 0.3082184275634954 T_1(x) + 0.0928329$$

$$274040524 T_2(x)) / (1 - 0.295912231995878 T_o(x)$$

$$+ 0.786296083825448 T_1(x) - 0.0687688789232632 T_2(x)))$$

$$+ 0.00661$$

$T_i(x)$  : Tchebyshev polynomials in  $x$



These relationships are considerably different from those used by Murtagh and Stott<sup>97</sup>. In their calculations, although the coal temperature reached 100°C, it never rose above this figure.

The program was used to determine the effect of diffusion and the correction for the perfect gas law. These computations will be discussed later, and as it was shown that the effect of diffusion and the correction for the perfect gas law was negligible, the computations were carried out without taking the diffusion of gases in the voids into account.

The results obtained for different rates of flow of the air are shown in Figures 30 to 45.

The difference in the liability of a pile of coal to fire when the air reached the vapour pressure when in equilibrium with a free liquid surface, and when the equilibrium vapour pressure in the air decreases with decreasing moisture content of the coal, is as explained earlier. It is significant that the later mechanism used in the calculations in this thesis predicted the firing of a pile of coal, whilst earlier calculations, assuming air saturated with moisture at all times, did not.

Appendix 6 gives a simplified calculation of the vapour pressures which can be sustained by the oxidation at different temperatures, when the coal has been oxidised to a certain degree. The process of development of a heating is tentatively suggested as follows. As an air current flows into the pile, the oxidation produces heat to raise the temperature and evaporate moisture to raise the humidity of the air to

equilibrium value at increasing temperatures. The temperature is gradually increased along the direction of the air current, until the oxygen in the air is completely depleted. Further into the pile, the moisture in the air is condensed, and raises the temperature to the highest value attained in the region where the oxidation takes place. It can be seen that this region gradually expands further as more moisture flows into it.

Where the last trace of oxygen is found, the temperature reaches its maximum. The rate of oxidation at this place does not have the highest value in the coal pile. The highest rate of oxidation, and hence the highest rate of evaporation of moisture initially is close to the surface, but gradually moves into the heap, until the maximum temperature attainable is reached. This maximum temperature is the temperature where the change in humidity with respect to temperature, starts increasing much faster than the change in rate of oxidation by temperature.

The place where the rate of oxidation is highest is then a function of temperature and oxygen concentration. It is close to the place where the maximum temperature is, because the rate is more sensitive to temperature than to oxygen concentration. Its position is changed because of the reduction of the rate of oxidation with the degree of oxidation and therefore the oxygen can reach further into the heap. The reduction of the rate of oxidation is caused by the decrease in temperature because of a decrease in the rate, and the increase in the degree of oxidation. However, it was found that the change in position of this place is only

slight from the time when the maximum temperature has been reached until the fire starts developing. (Figures 30, 34, 38, 42).

It can be seen that as the molecular processes are negligible in the range of rates of flow from 1 cc/cm<sup>2</sup>min to 20 cc/cm<sup>2</sup>min, the equation of continuity and the energy equation can be rewritten as follows:

$$\frac{\partial}{\partial t} (\rho_i w_i) \approx - \frac{\partial}{\partial X} (\rho_i w_i) + r_i$$

$$C_1 \rho_1 \frac{\partial T}{\partial t} \approx \frac{dQ}{dt} - C_2 \rho_2 \frac{\partial T}{\partial X} - \Delta H_{H_2O} r_{H_2O}$$

where  $r_{H_2O} = Vf(\frac{\partial T}{\partial x}, \frac{\partial W}{\partial x})$

$$= f(\frac{\partial T}{\partial X}, \frac{\partial W}{\partial X})$$

$$X = \frac{x}{V}$$

$W$  = moisture content

$T$  = temperature

$V$  = velocity

The function  $f(\frac{\partial T}{\partial x}, \frac{\partial W}{\partial x})$  is the same for different rates of flow only when the equilibrium vapour pressure is attained. Therefore in this case, the location and the size of the place where the fire takes place have constant values in  $X$ , and therefore are directly proportional to the rate of flow. The time when the fire starts is independent of  $X$ , and therefore does not depend on the rate of flow.

However, equilibrium probably can be attained only at very low rates of flow, therefore there are rates of flow where the above relationships do not hold. The temperatures are also

changed, and therefore the drying time will be much affected by the oxidation and the rate of drying (see Appendix 6). Therefore when equilibrium is not reached the distance from the surface of the place where the fire takes place, and the dimensions of the fire, are not directly proportional to the rate of flow of the air current.

It can be seen that, when the length of the pile along the direction of the air current is less than the distance from the surface to the place where the fire would have taken place for the rate of flow of the air, the pile can be considered as safe. For example, from Figure 42, it can be seen that an air current of  $20 \text{ cc/cm}^2\text{min}$  will increase the temperature of a pile 16 m long to the highest value of  $70^\circ\text{C}$  after 80 hours, then the rate of heating starts decreasing. It can be seen from Figure 45 that the moisture content of the coal is still relatively high for the 16 m length section, therefore there is no possibility that the drying can continue at some intermediate temperature as in a region of lower moisture content, and the temperature therefore decreases to that of the ambient temperature.

Therefore, if the amount of air leakage into a pile of coal, caused by ventilation, can be found, the safe quantity of ventilation can be obtained for the dimensions of the pile.

#### Effect of Diffusion of Gases Through Voids in the Coal Bed

The effect of diffusion of oxygen is negligible when the rate of flow is large. It can be seen from the following simplified example:

Consider the diffusion equation:

$$N = D \frac{\partial C}{\partial x}$$

Assume a concentration of 21 percent/100 cm which is  $0.27 \times 10^{-5}$  gm of  $O_2/cm^4$ .  $D$  can be approximated by the binary diffusion coefficient of air-oxygen mixture, which is equal to  $0.178 \text{ cm}^2/\text{sec}$ . The rate of flow due to diffusion is  $1.73 \times 10^{-4}$  gm/cm<sup>2</sup>hr, which is equivalent to a flow of air of  $6 \text{ cc/cm}^2\text{hr}$ , or approximately 10 percent of a flow of  $1 \text{ cc/cm}^2\text{min}$ .

It was thought that local drying by diffusion due to difference in vapour pressure, although small, may critically speed up the drying of the coal, since the region of lowest moisture content usually has the highest temperature. Consider a flow of  $1 \text{ cc/cm}^2 \text{ min}$ . The temperature curves are shown in Figure 30. At 100 hours, the maximum temperature is  $92^\circ\text{C}$  at 2.5 m from the surface. The moisture contents, as shown in Figure 33 are still above the saturation points of this range of temperatures. The humidity gradient is therefore

$$\frac{(0.65 - 0.585) \text{ gm/gm}}{15 \text{ cm}}$$

The diffusion coefficient of the air - water vapour mixture is  $0.22 \text{ cm}^2/\text{sec}$ , therefore the flow of moisture due to diffusion is  $4.5 \times 10^{-3}$  gm/cm<sup>2</sup> hr, therefore the rate of drying by diffusion is approximately 2.9 percent of moisture/100 hrs over a region of 15 cm length.

However, it can be seen from the temperature curves that the gradients change continuously during the drying period, therefore there is no region which is continuously

being dried by diffusion, and the cumulative effect of drying by diffusion is therefore not as pronounced as shown in the example above.

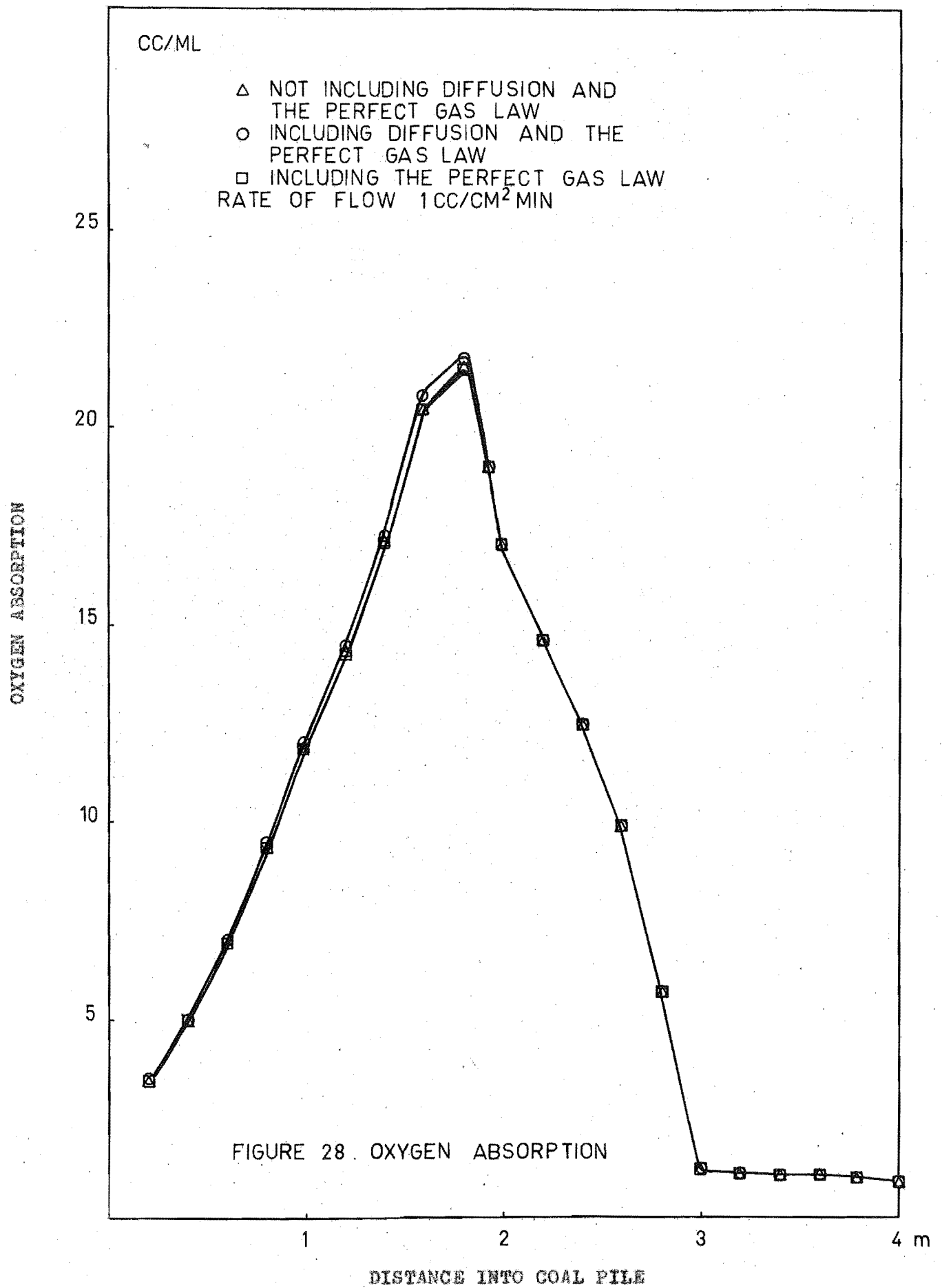
In order to check the effect of diffusion of water vapour, oxygen and nitrogen, calculations were carried out with and without the equations governing diffusion. The results are shown in Figures 28, 29, which show the effect in these calculations to be negligible. It can be seen that diffusion of the gases should be included only for rates of flow less than  $0.5 \text{ cc/cm}^2\text{hr}$ , and when the drying time is more than 500 hours.

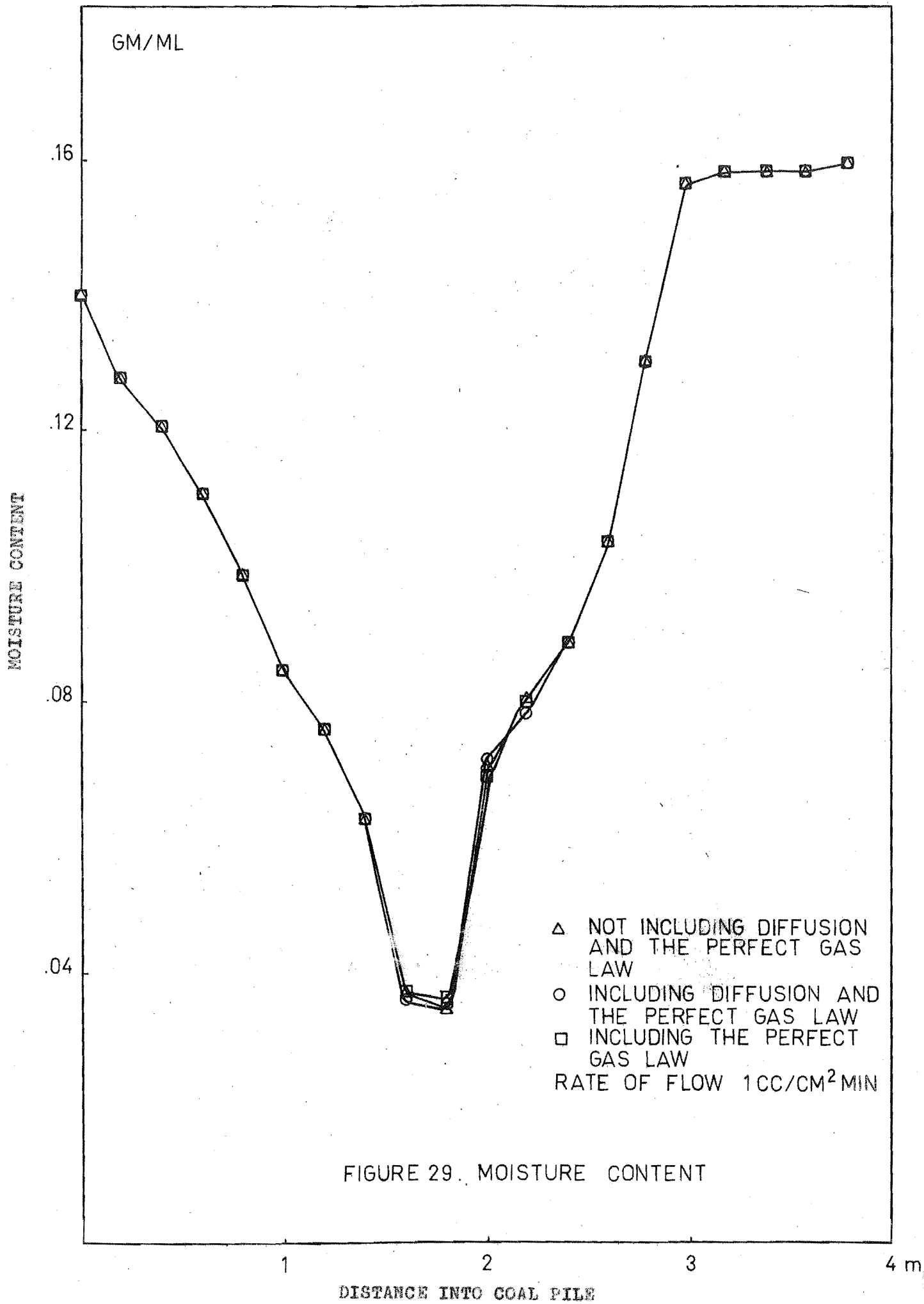
#### The Effect of the Perfect Gas Law

The perfect gas law has an effect on the rate of flow. Consider a flow of  $1 \text{ cc/cm}^2\text{min}$  at N.T.P. into a section of 100 cm length initially at  $80^\circ\text{C}$  and rises to  $90^\circ\text{C}$  in 1 hour. The increase in the flow due to the expansion of the air in the voids is therefore equal to  $100 \times 0.46 \times \frac{10}{353} = 1.3 \text{ cc/hr.cm}^2$ , which is approximately 2 percent of the total flow.

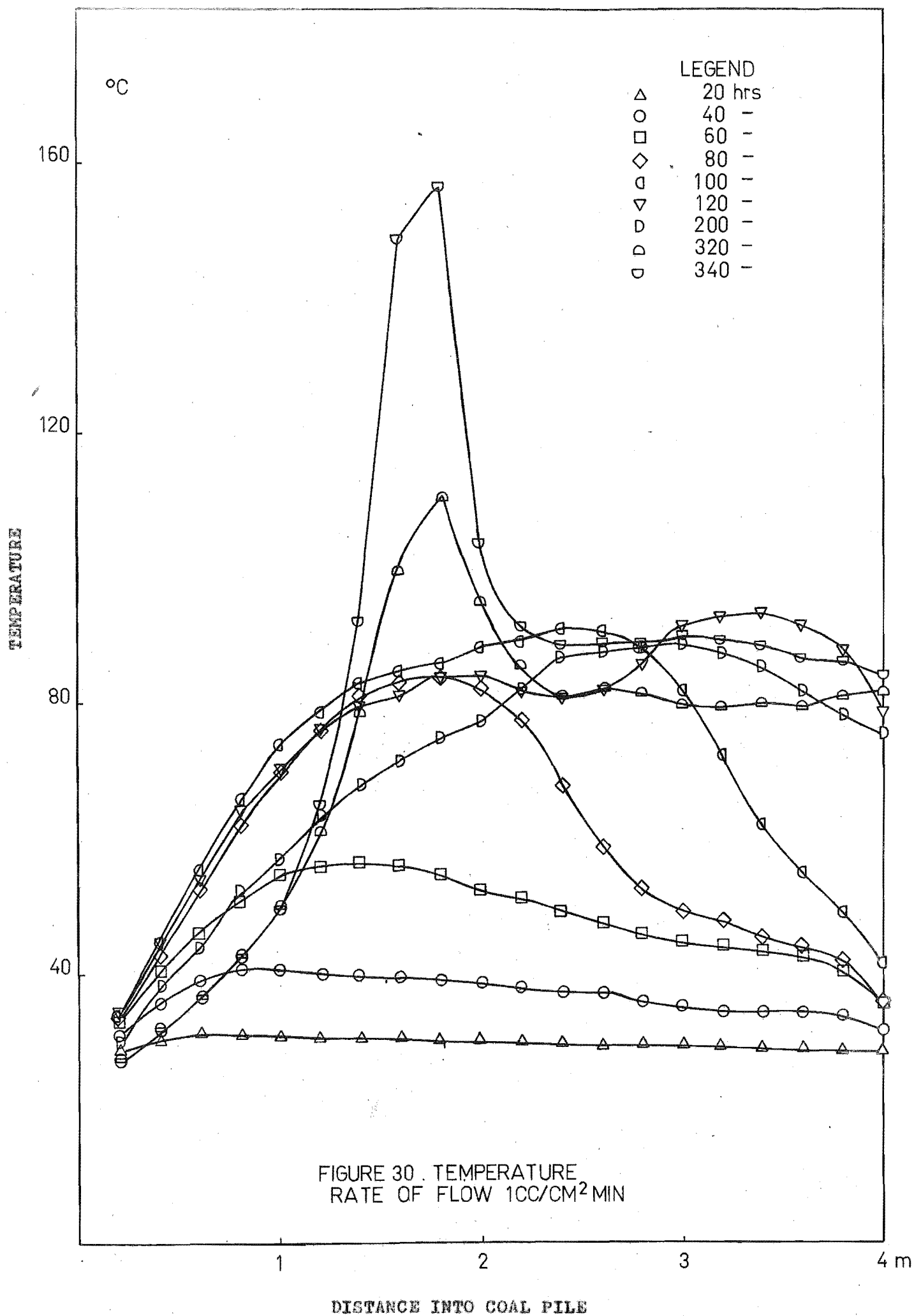
From Figures 30, 34, 38 and 42 it can be seen that in the region where the oxidation and drying take place, the temperatures are relatively constant after the initial heating stage. Therefore the perfect gas law does not have an appreciable effect on the heating.

The effects of the correction for the perfect gas law are shown on Figures 28 and 29. It can be seen that they are negligible.









PARTIAL PRESSURE  
ATS.

FIGURE 31. OXYGEN CONCENTRATION  
RATE OF FLOW 1CC/CM<sup>2</sup> MIN

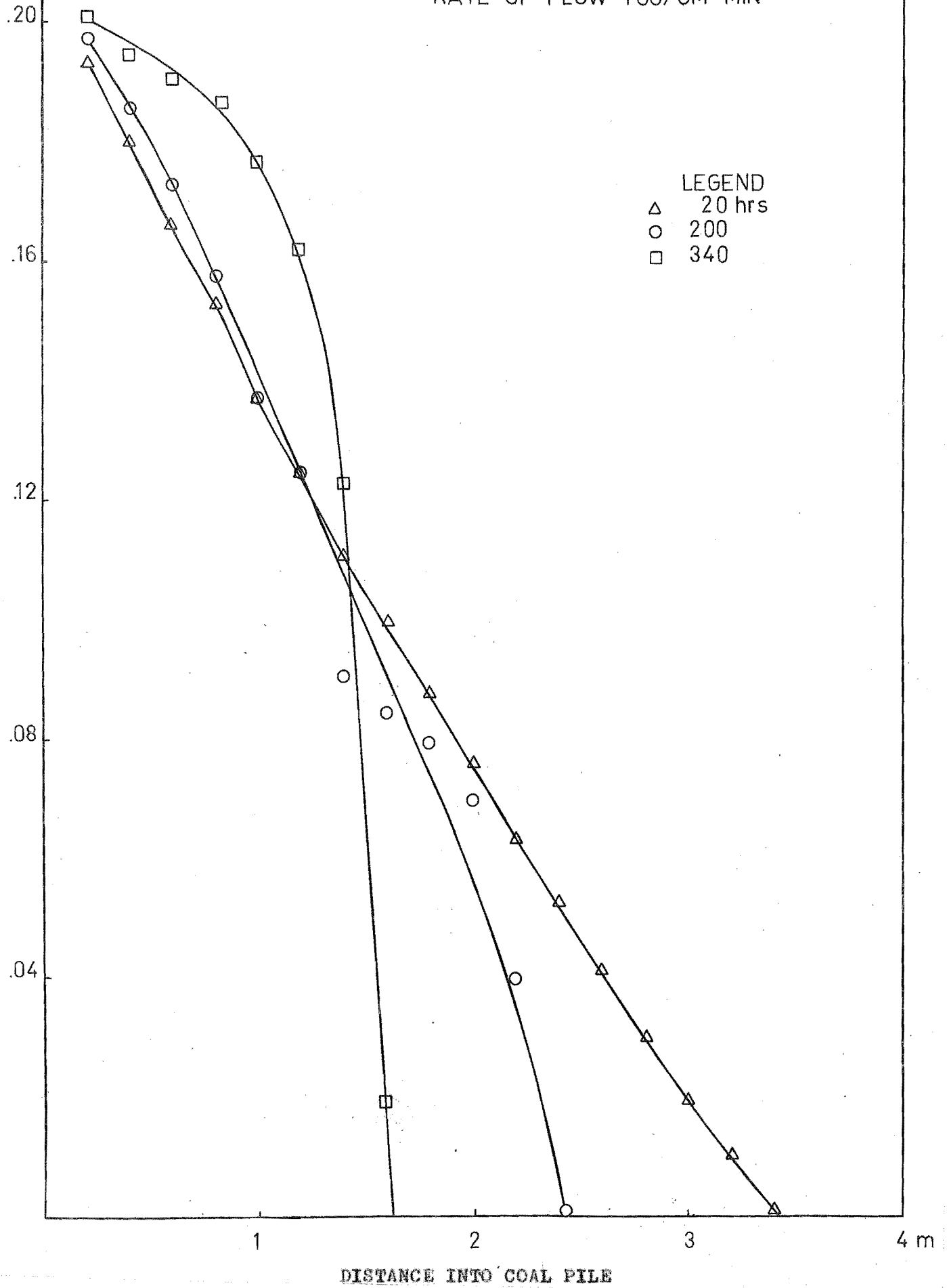


FIGURE 32. OXYGEN ABSORPTION  
RATE OF FLOW 1CC/CM<sup>2</sup> MIN

CC/ML

LEGEND

- △ 100 hrs
- 200 -
- 320 -

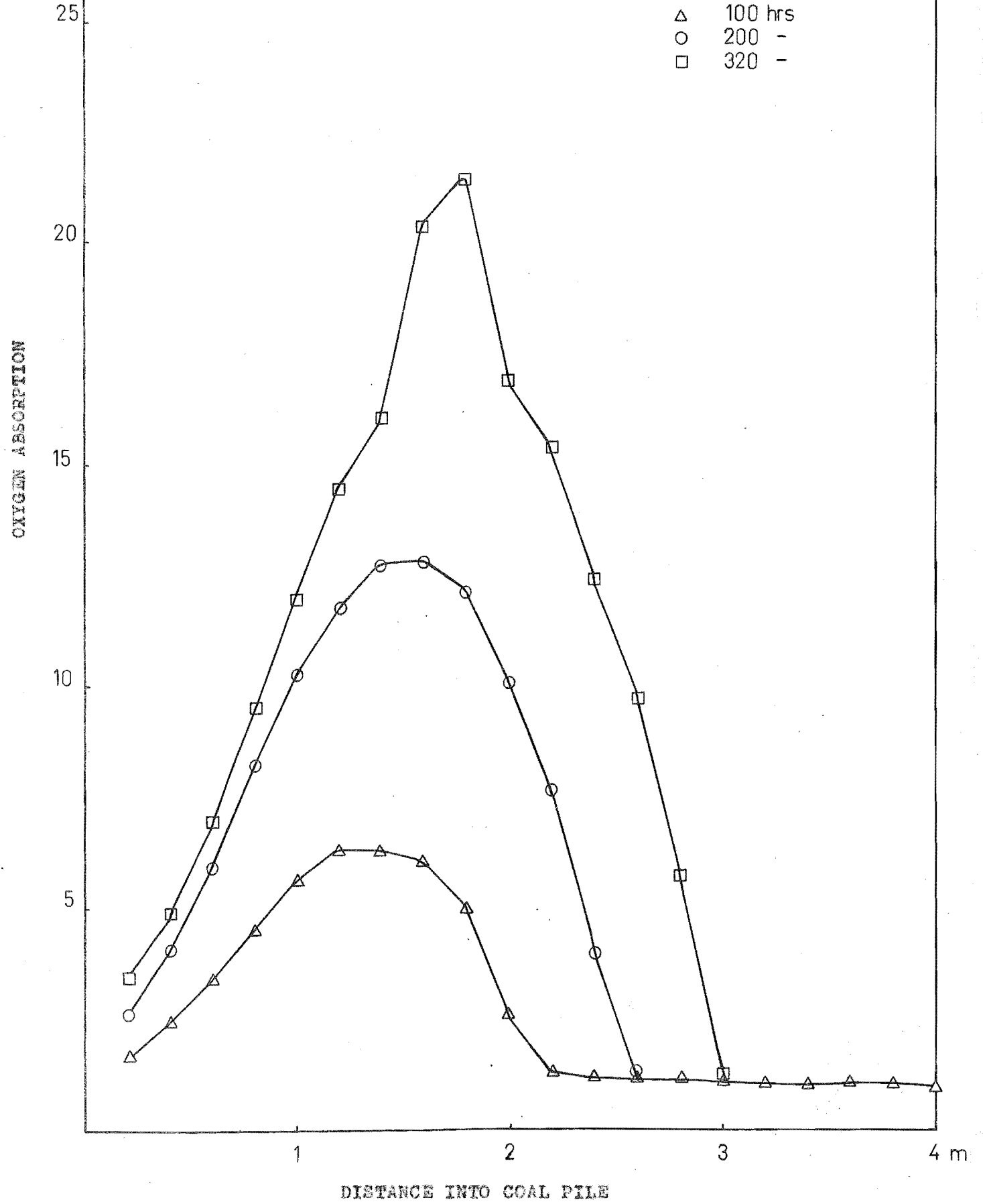
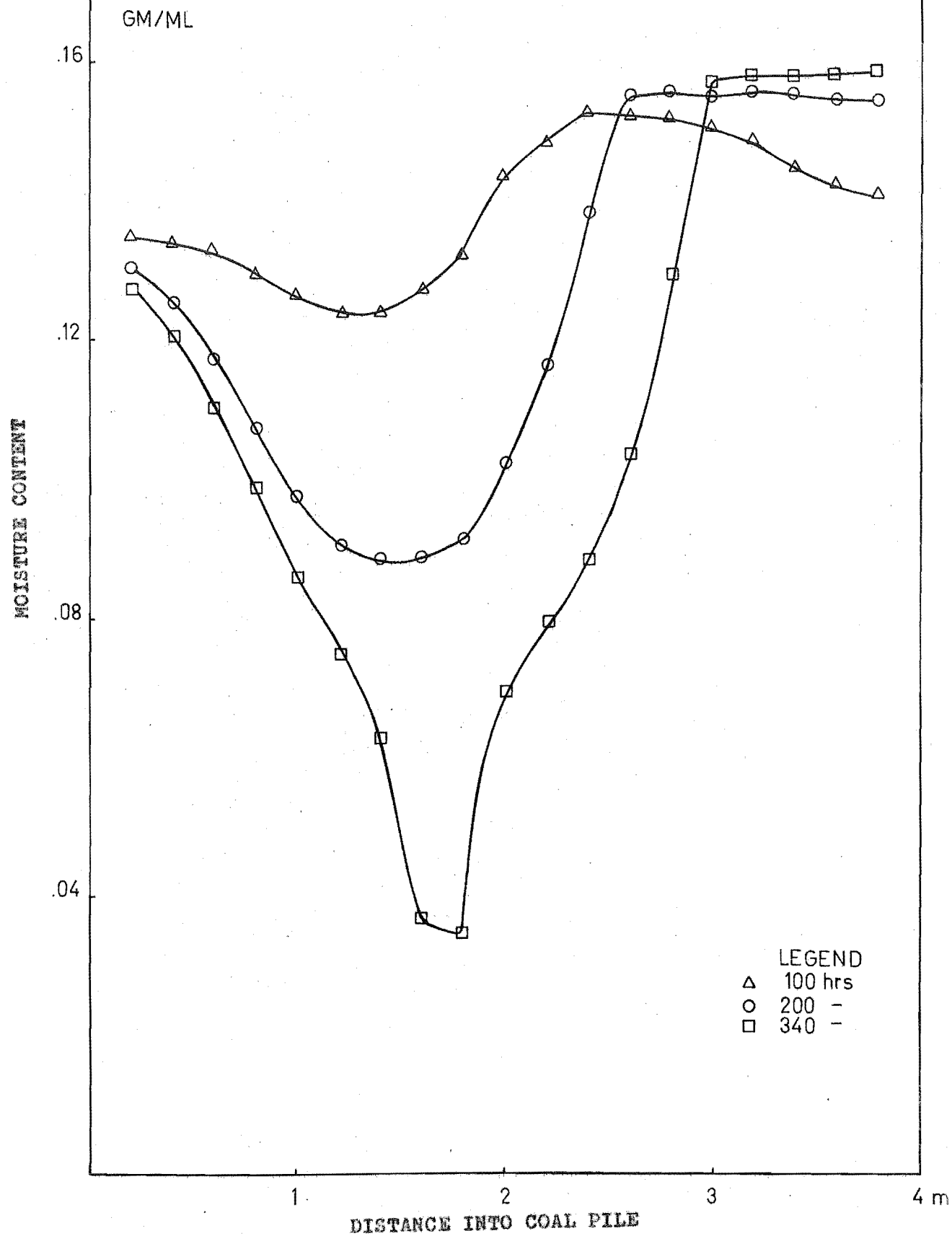
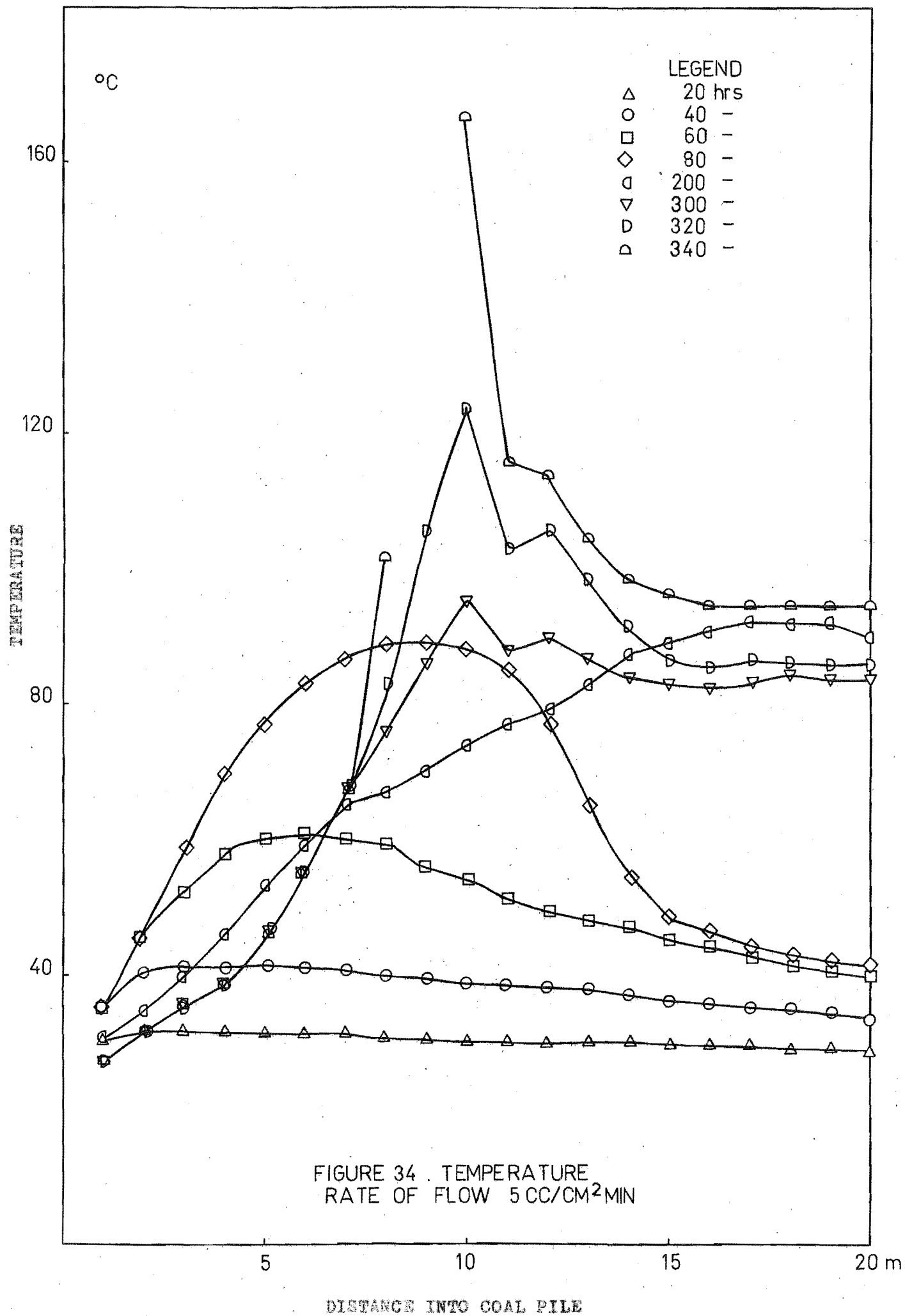


FIGURE 33. MOISTURE CONTENT  
RATE OF FLOW 1CC/CM<sup>2</sup> MIN





PARTIAL PRESSURE  
ATS.

FIGURE 35. OXYGEN CONCENTRATION  
RATE OF FLOW 5 CC/CM<sup>2</sup> MIN

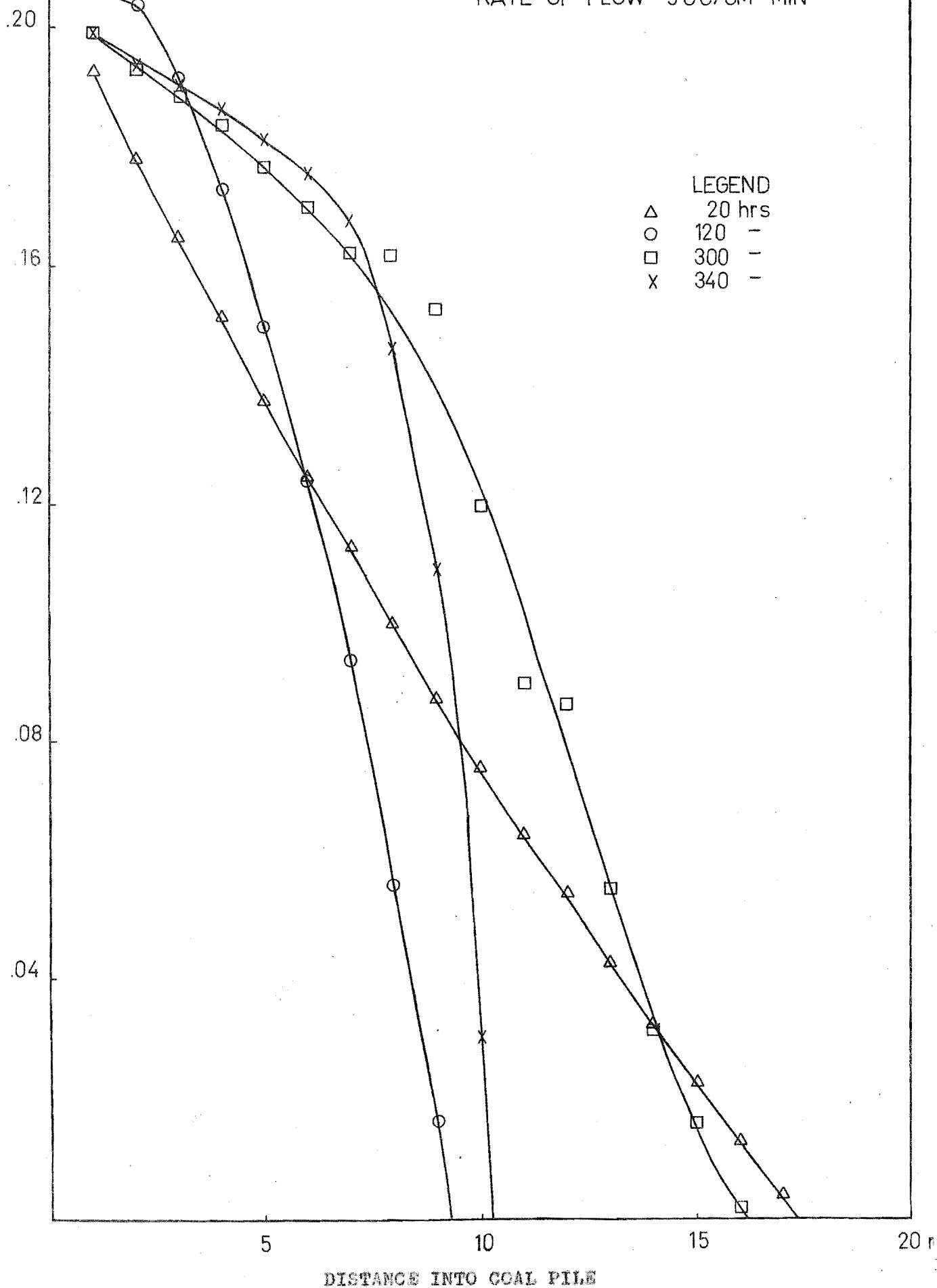


FIGURE 36. OXYGEN ABSORPTION  
RATE OF FLOW 5CC/CM<sup>2</sup>MIN

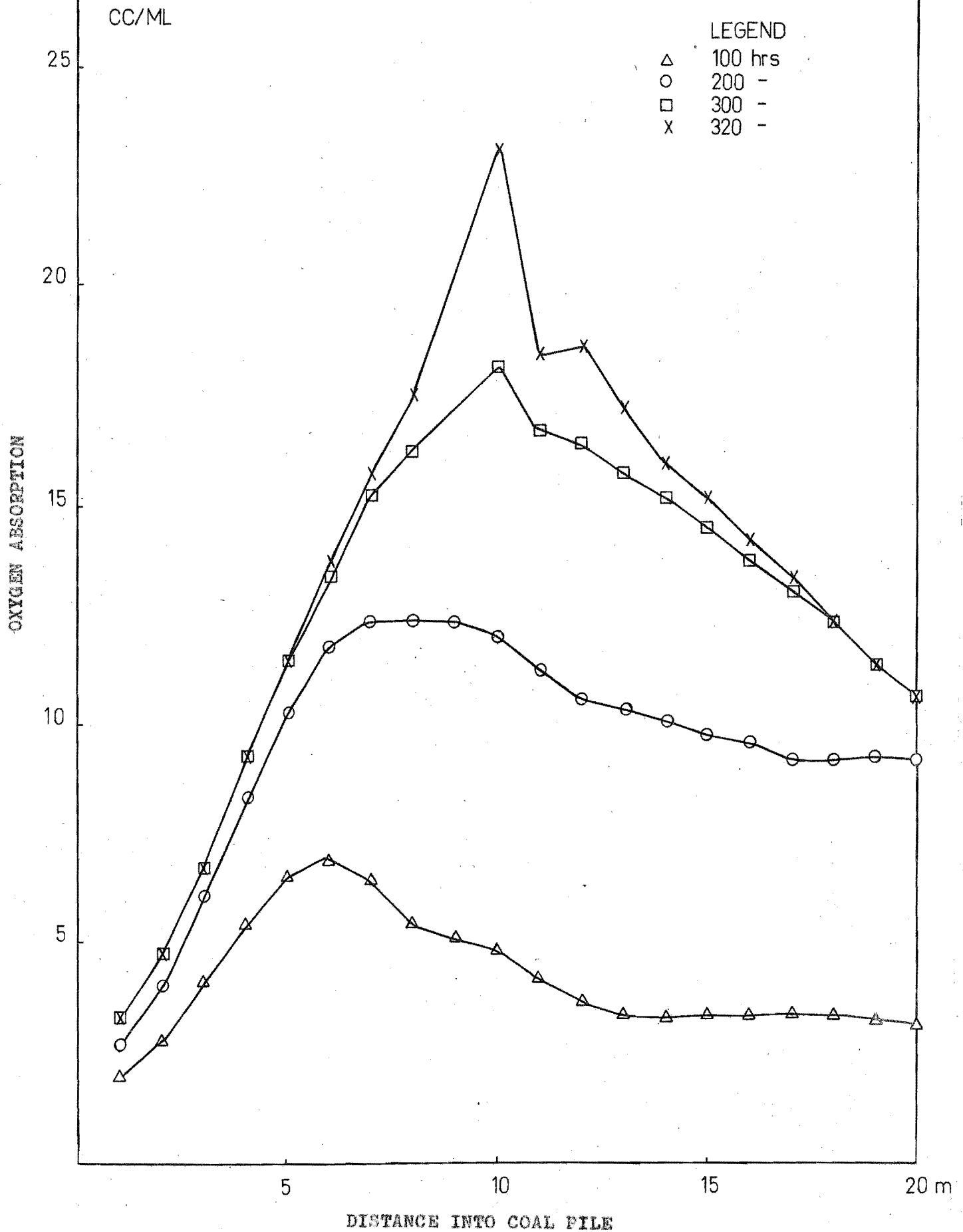
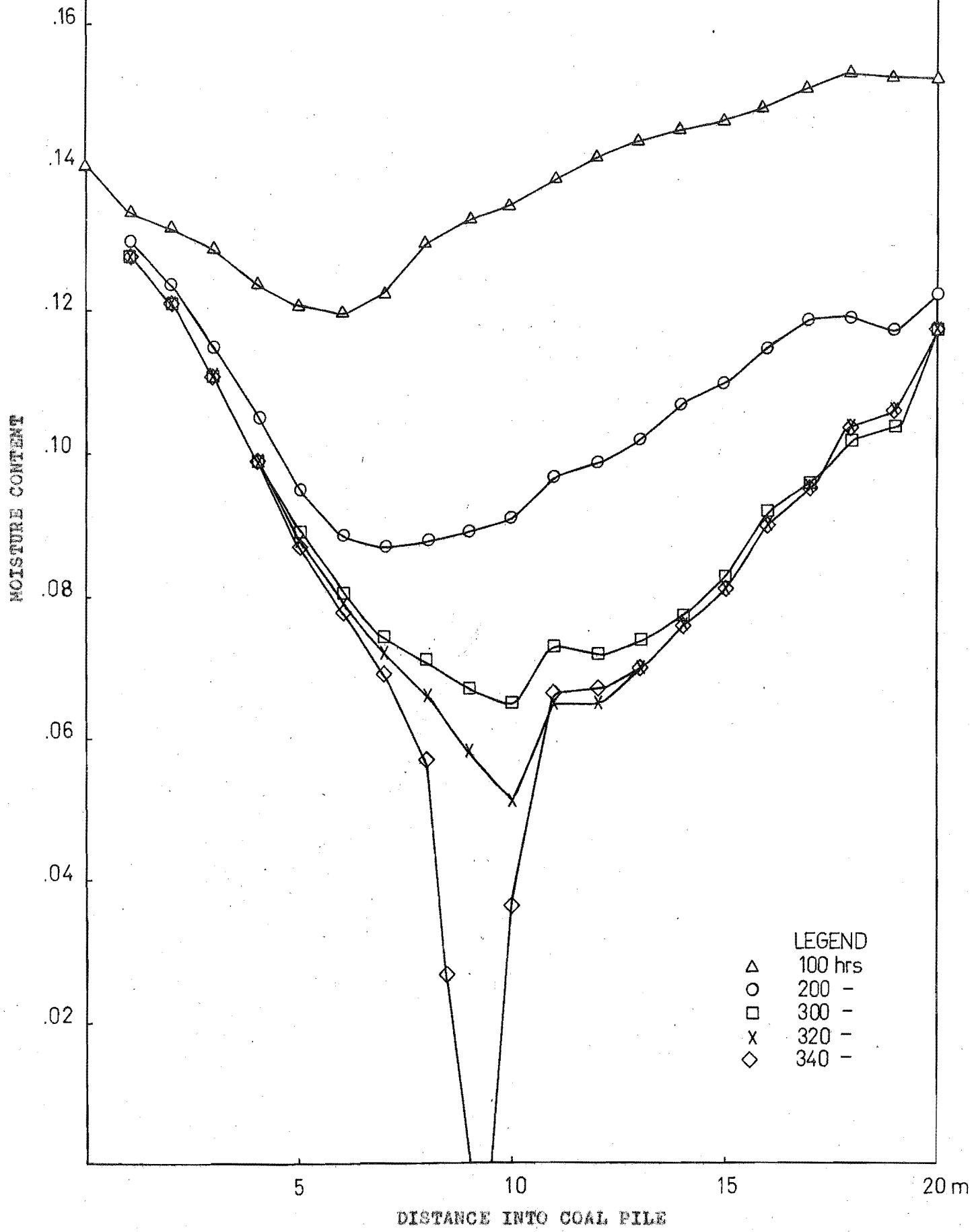
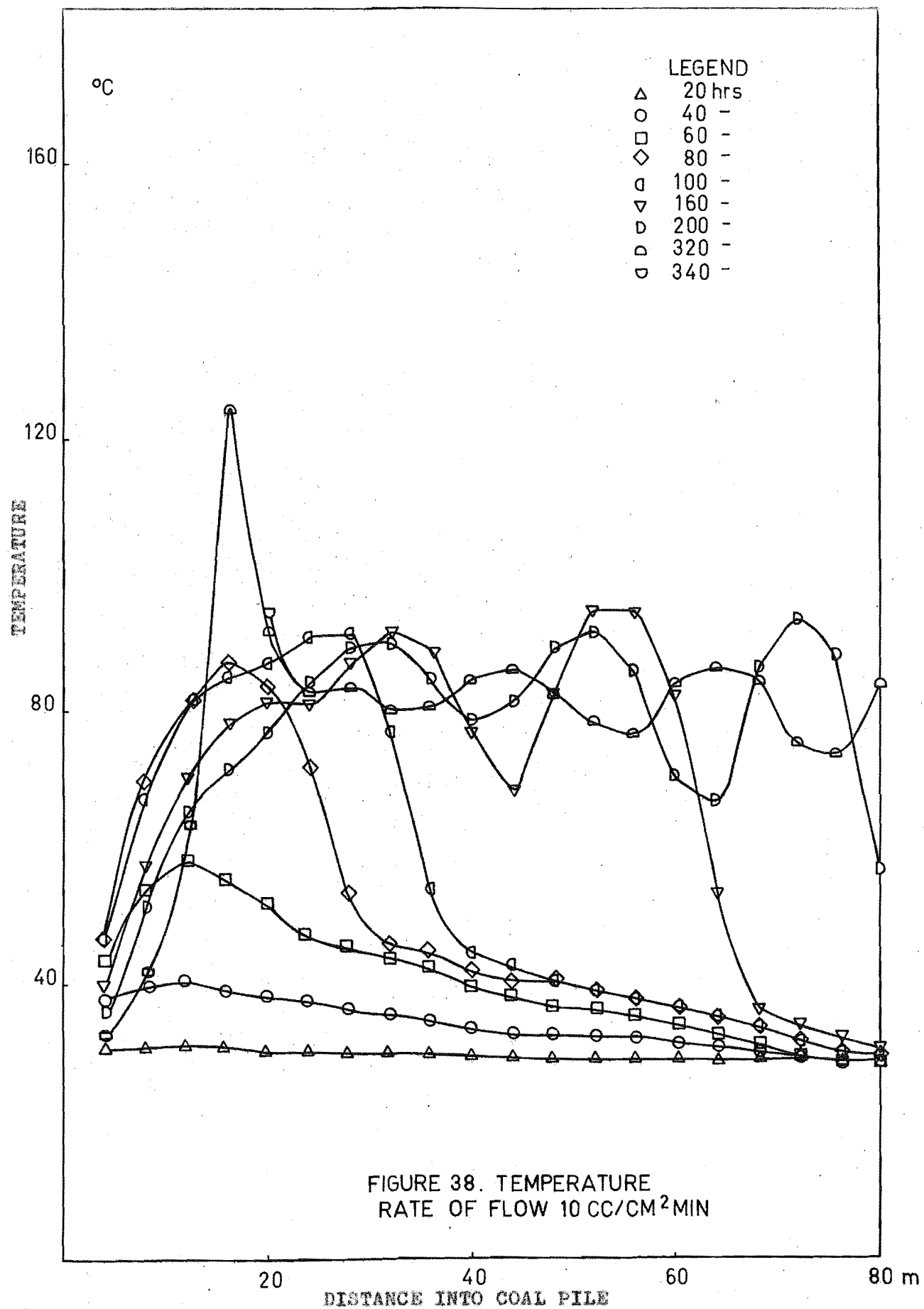


FIGURE 37. MOISTURE CONTENT  
RATE OF FLOW 5CC/CM<sup>2</sup>MIN

GM/ML







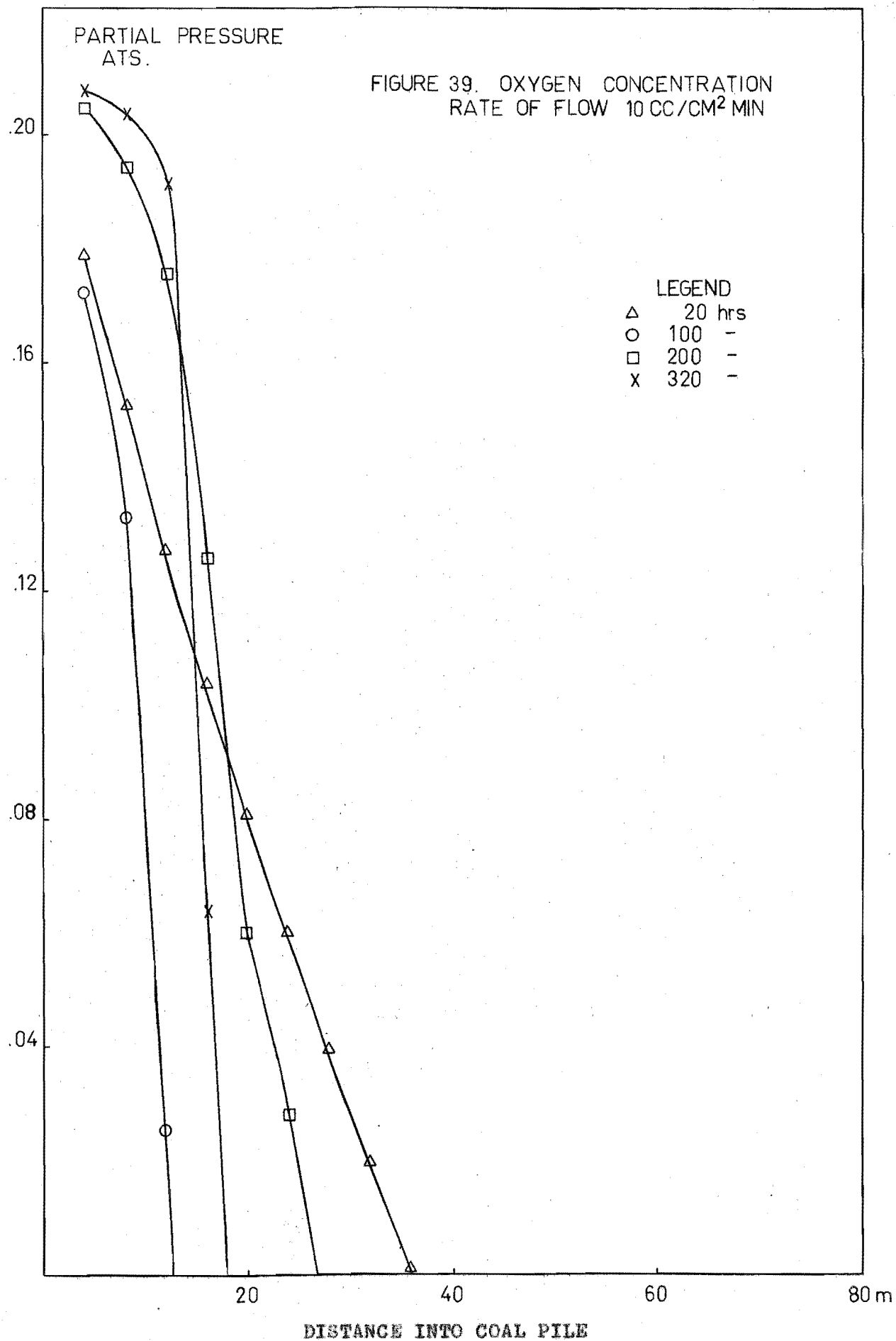


FIGURE 40. OXYGEN ABSORPTION  
RATE OF FLOW 10 CC/CM<sup>2</sup> MIN

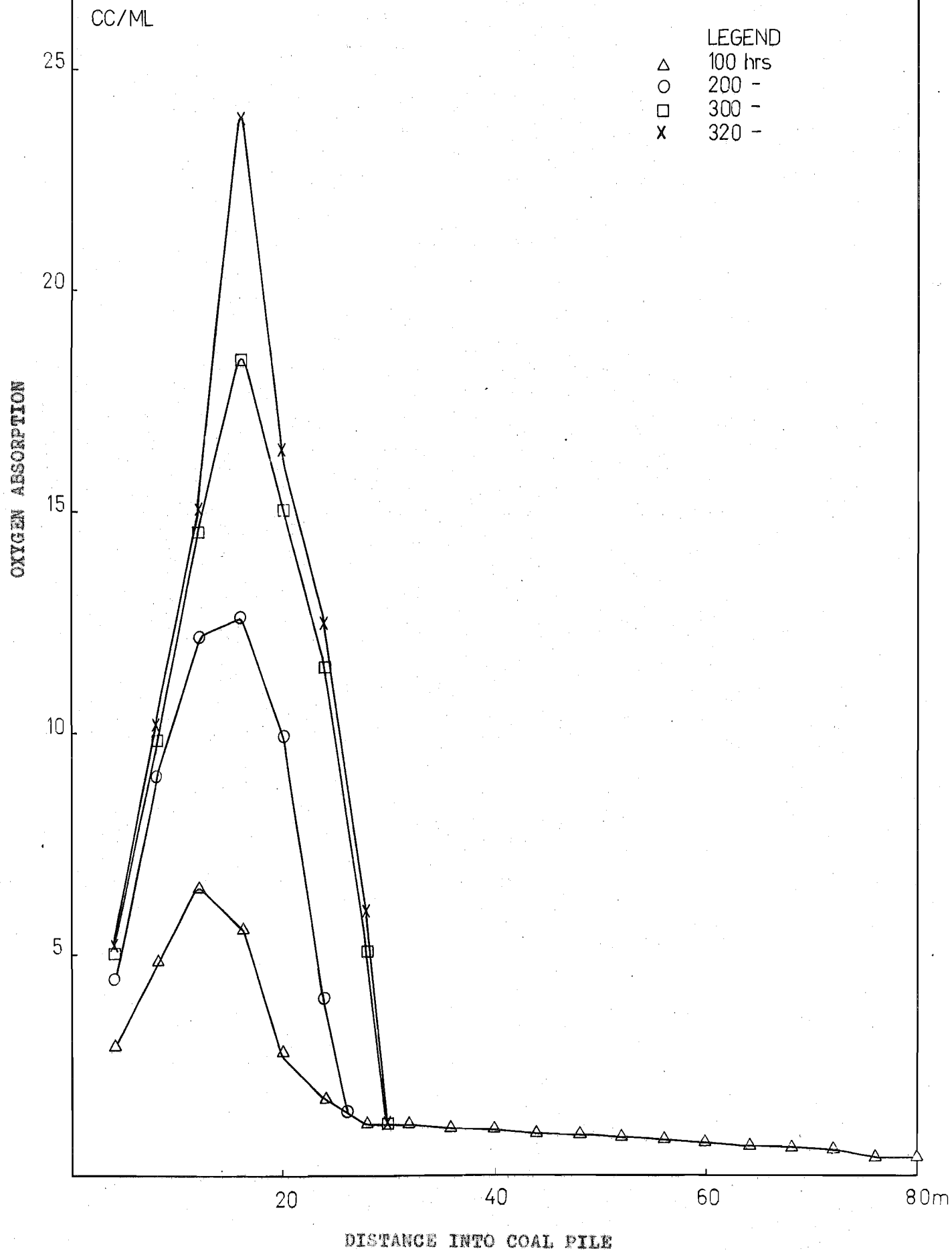
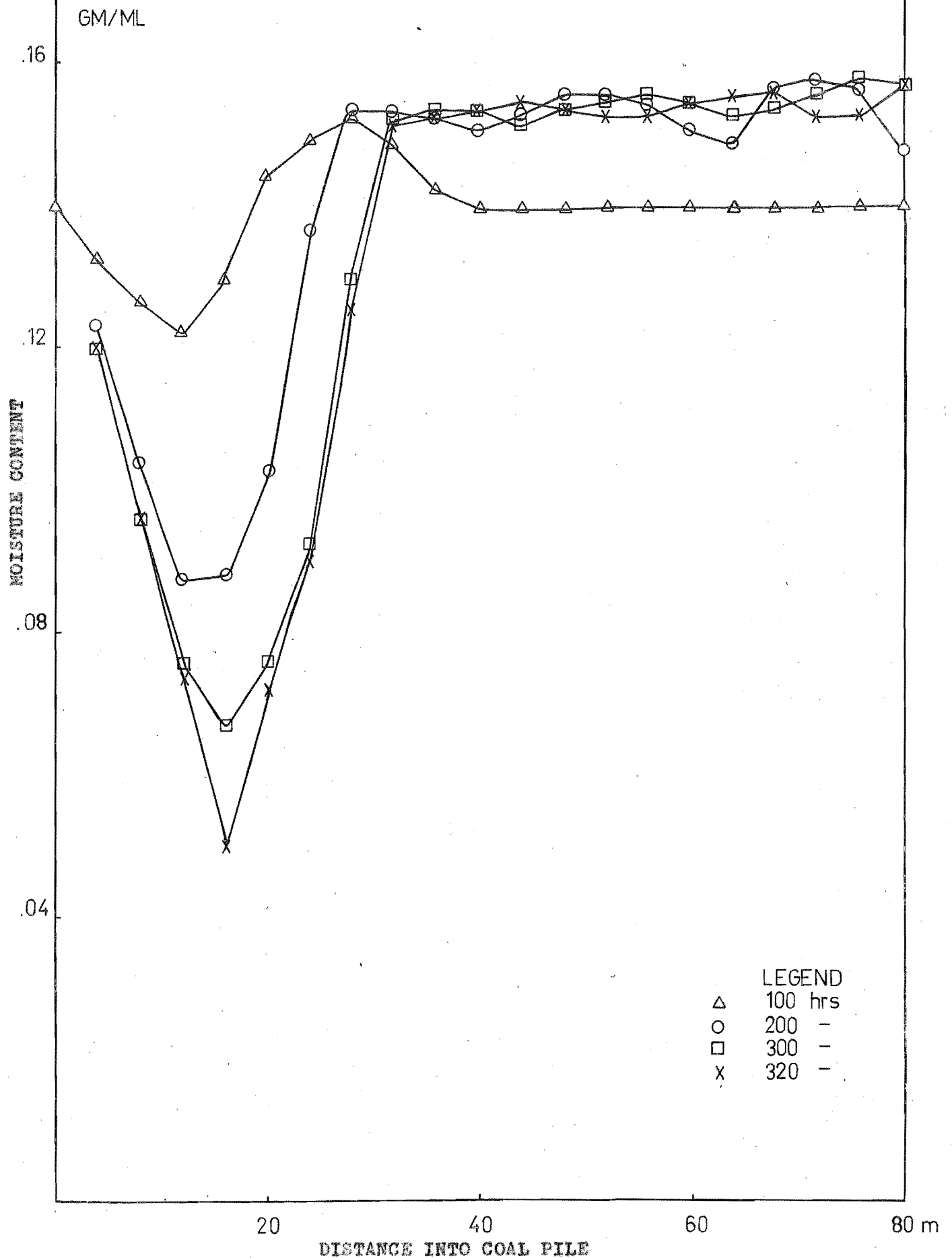
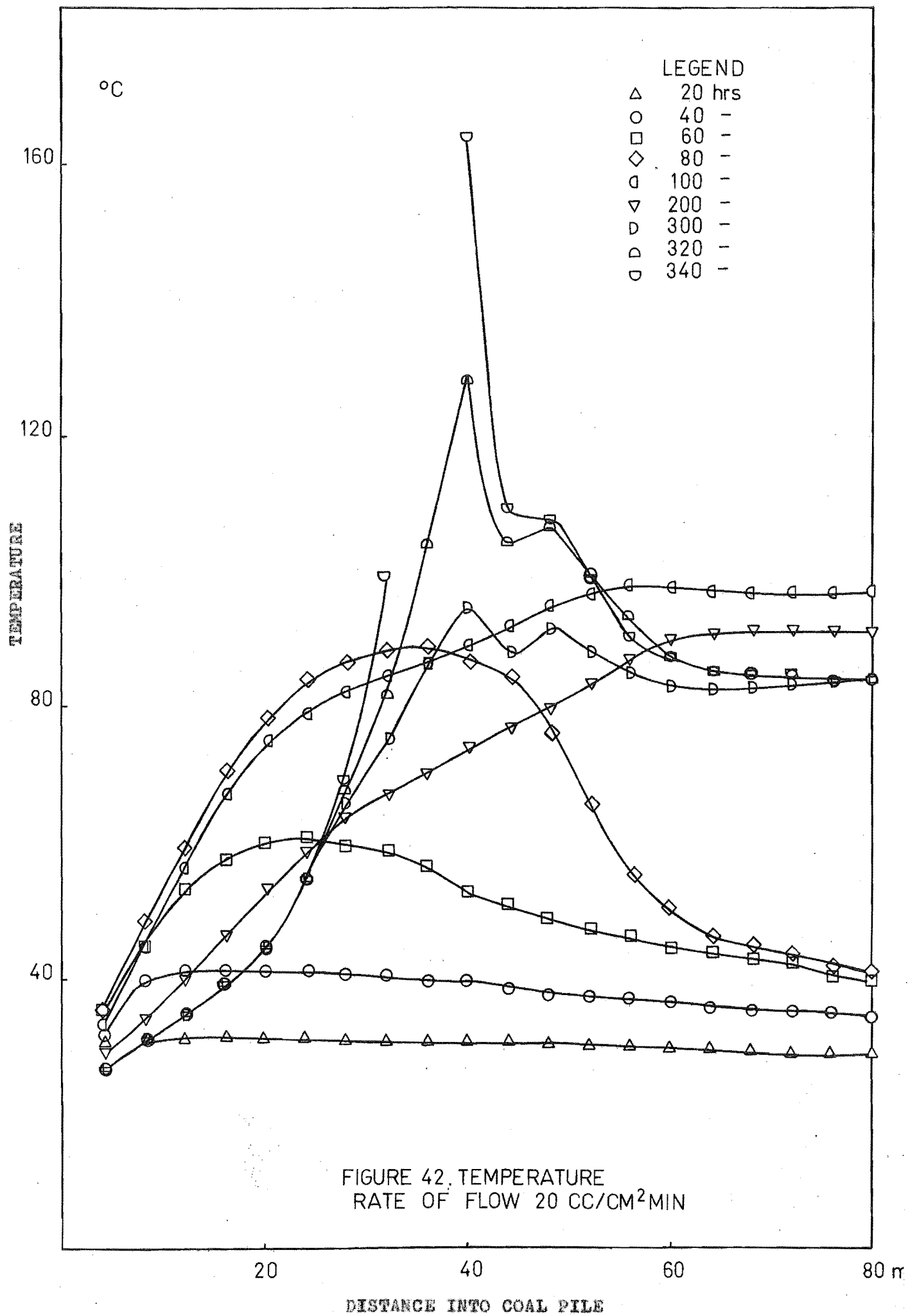


FIGURE 41. MOISTURE CONTENT  
RATE OF FLOW 10 CC/CM<sup>2</sup> MIN





PARTIAL PRESSURE  
ATS.

FIGURE 43. OXYGEN CONCENTRATION  
RATE OF FLOW 20CC/CM<sup>2</sup> MIN

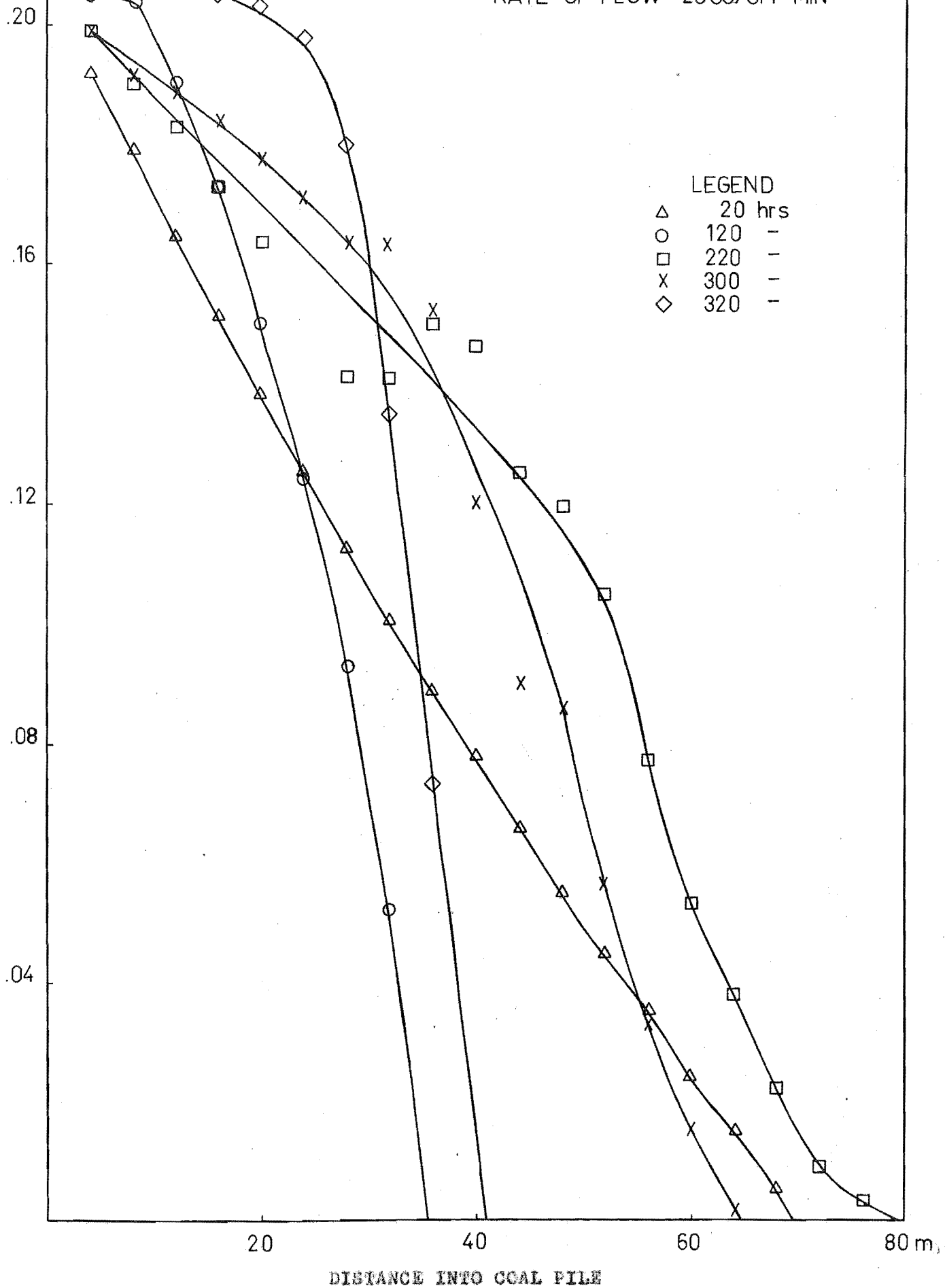


FIGURE 44. OXYGEN ABSORPTION  
RATE OF FLOW 20 CC/CM<sup>2</sup> MIN

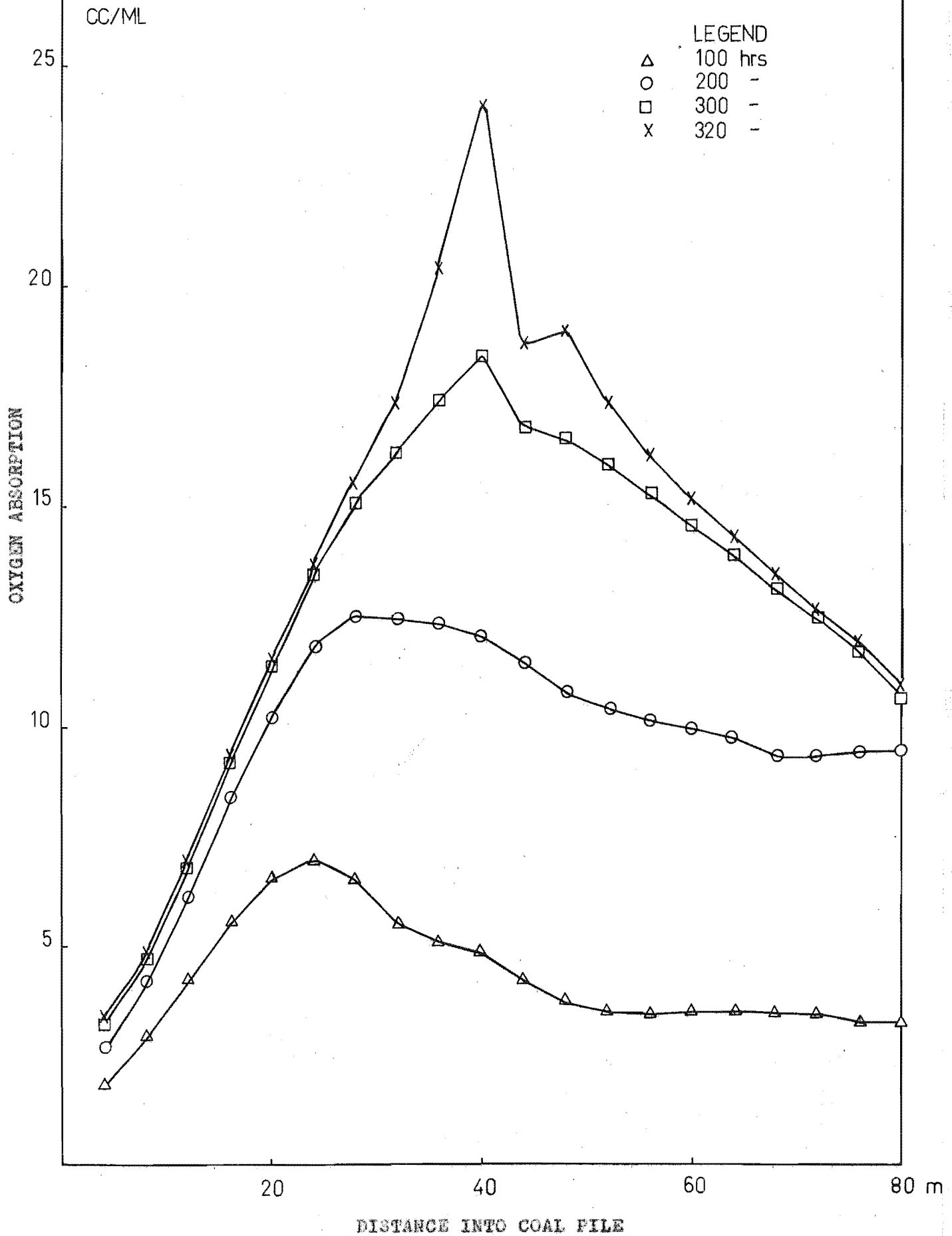
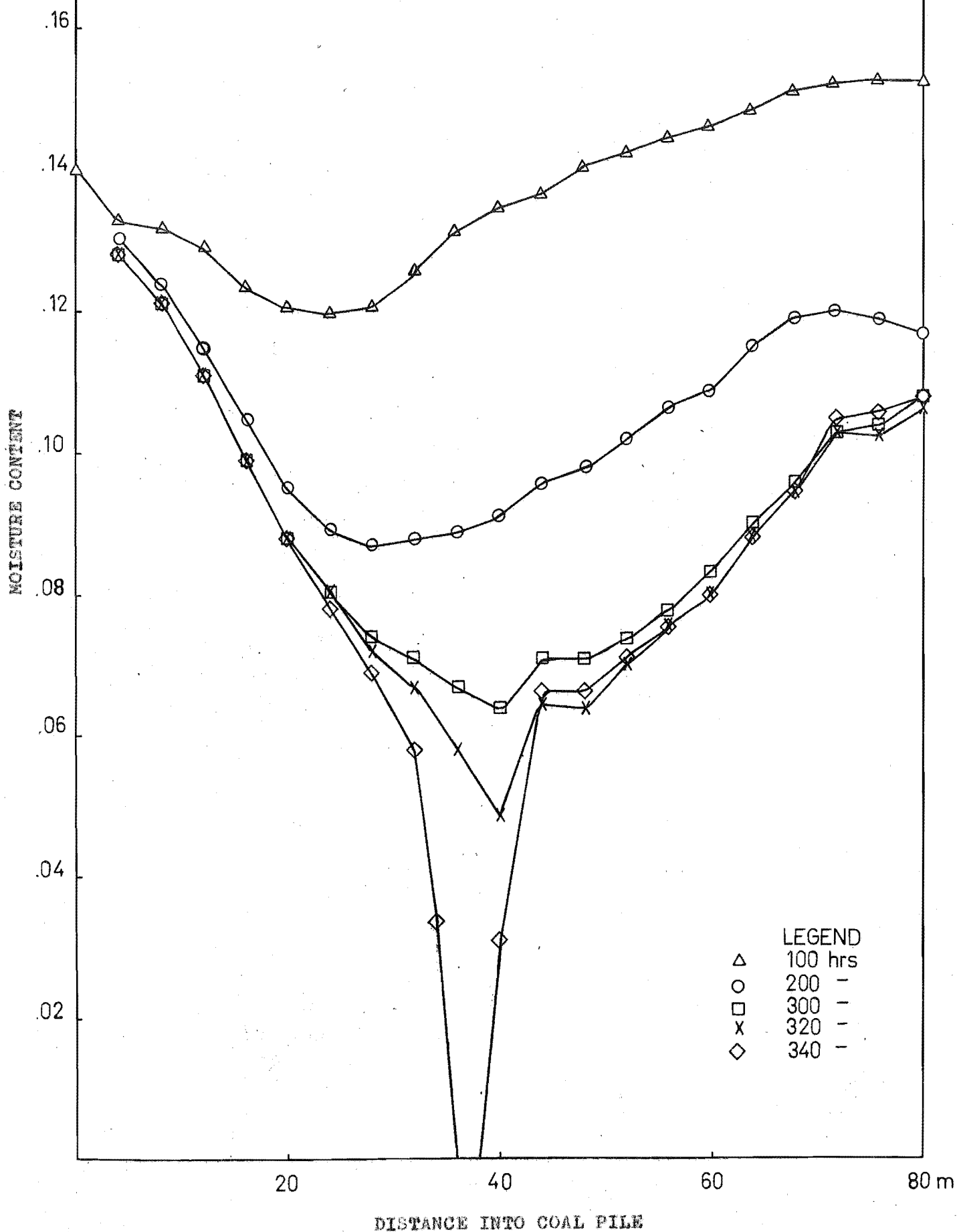


FIGURE 45. MOISTURE CONTENT  
RATE OF FLOW 20 CC/CM<sup>2</sup> MIN

GM/ML





### The Smallest Size of Piles Which Are Susceptible to Fire

It has been shown from practical observations that, in underground mines, only piles of coal that are over five feet are usually liable to fire. As freshly mined low rank coals have a relatively high moisture content, for a given rate of air leakage, the dimensions of the pile must be greater than a minimum value so that a hot spot can develop. For dry coals, a fire can develop in a location much closer to the surface, and the dimension of the hot spot can be much smaller because there is no heat loss by evaporation. Under these conditions the coal reaches a high temperature when it is still more reactive compared with heating in a wet coal which must be dried before it can reach a high temperature. At the point which has the maximum heat available to raise the temperature of the coal, the growth of the hot spot is fast, and it can be shown that as the hot spot develops, the heat loss is mainly by conduction and the more reactive the coal is, the smaller the dimension of the hot spot needs to be. It has been observed that the dimension of the fire in dry coal can be small, of the order of 2 inches<sup>93</sup>, and hot spots which develop at a distance 1 ft from the surface have often been found in storage piles<sup>1</sup>, because the coal is drier than that freshly mined.

These figures suggest the possibility that diffusion of gases in the voids may cause coals which are reactive and dry to fire. A study of diffusion of gases in a stationary system should take into account that it may not be able to simplify the process into equivalent binary diffusion processes as has been done in our programme, and there is a net flow

which arises from the unequal diffusional flows of the components and the oxygen depletion.

The possibility may never happen in practice since coals which are reactive also contain a considerable amount of moisture, in which case heating can only occur when a flow, larger than that arisen from diffusion, is passed through the pile. In storage piles, the moisture content of coal is usually lower than that of the run of mine coal, the percentage of fires is higher because of the slacking property. However, the coal is also more weathered than that in piles in underground mines.

Diffusion of moisture in a pile of coal is small. It has been observed that moisture content of coal at further than 3 inches from the surface remains constant<sup>26</sup>. The simultaneous energy and moisture transfer equations of moisture transfer in hygroscopic materials have been studied by Henry<sup>56,57,13,19</sup>. It was shown that when the external conditions of a pile of the material are changed, the heat of sorption causes a temporary equilibrium state, and the permanent equilibrium conditions in the pile are only reached much more slowly.

When all the moisture has been evaporated, the temperature of the hot spot starts to rise much faster than its surroundings. The heat loss at this stage is mainly by conduction. The energy equation of the hot spot can therefore be written as

$$C_p \frac{\partial T}{\partial t} = q - \lambda \nabla^2 T$$

where  $q$  = heat generation/unit volume

$\lambda$  = thermal conductivity

Approximate analytical solutions for the critical dimension of the hot spot have been obtained for the case when  $q$  varies with temperature only<sup>29</sup>, and when  $q$  also decreases according to a gaseous reaction of order  $n$  as the reactant is consumed<sup>99</sup>.

Using the results obtained by the calculations, the approximate value of the minimum dimension of the hot spot can be found from these solutions. The heat loss by conduction in the stages prior to this stage is still negligible. Therefore the following results, which are obtained from Figures 30 to 45, hold:

1. The distance of the hot spot from the surface is approximately equal to 2 metres x rate of flow ( $\text{cc}/\text{cm}^2\text{min}$ ).
2. The dimension of the hot spot is approximately equal to 40 cms x rate of flow ( $\text{cc}/\text{cm}^2\text{min}$ ).
3. The moisture content of the surrounding regions is still at a high value, therefore the temperature of the surrounding regions is at a constant value while the temperature of the hot spot rises. It is assumed to be at  $100^\circ\text{C}$ .
4. The quantity of oxygen which has been absorbed by the coal at the hot spot is the same as that for higher rates of flow. Therefore the quantity of oxygen absorbed to this stage is approximately 30 cc  $\text{O}_2$ /ml of coal bed.
5. The oxidation at the region in front of the hot spot can be considered as constant. Therefore the oxygen concentration of the air which enters the hot spot can be considered to be constant during this stage. From the

results obtained for higher rates of flow, this concentration is 12 percent. Assume that the average oxygen concentration at the hot spot is 5 percent.

The parameter  $\delta$ , defined as<sup>29</sup>:

$$\delta = \frac{Q}{\lambda} \frac{E}{RT_o^2} r^2 z e^{-\frac{E}{RT_o}}$$

where  $T_o$  = temperature of the surrounding regions is therefore

$$\delta = r^2 \times \left\{ \frac{3}{1.2} \times \frac{0.7}{100} \times \frac{1.445 \times 10^{13} e^{-\frac{8572.3}{373.0}}}{(1 + 0.022 \times 30 \times \frac{100}{0.7})^{0.895}} \right. \\ \left. \times \frac{8572.3}{373.0 \times 373.0} \times \sqrt{\frac{0.05}{0.21}} \right\}$$

The critical value of  $\delta$  for solid between two parallel planes has been found to be<sup>29</sup>:

$$\delta_{cr} = 0.88$$

Therefore the critical value of  $r$  is

$$r = 8.5 \text{ cm}$$

which is the minimum dimension of the hot spot. The maximum temperature rise in a hot spot which is slightly smaller than this critical dimension is<sup>29</sup>:

$$\Delta T = 1.2 \frac{RT_o^2}{E} \\ = 19^\circ\text{C}.$$

The amount of oxygen absorbed when the temperature has increased by this amount is 34.5 cc/ml. The rate is changed by a factor of 0.88. Therefore the errors arising from the assumption that the rate is not changed by the absorption of oxygen are small.

The rate of air leakage is therefore approximately  $0.2 \text{ cc/cm}^2\text{min}$  and the minimum dimension of the pile of coal where a fire can develop is therefore approximately 2 feet.

However, the rate is limited by the rate of flow of the air current until other factors, such as the chimney effect, become appreciable and change the rate of flow of the air current. Therefore if the rate during this stage is assumed to be the same in the hot spot, and does not increase with temperature, the value of  $q$  is:

$$q = \frac{3 \times 1 \times 60 \times 0.12}{40} = 0.54 \text{ cal/cc hr.}$$

If the criterion is that the temperature must increase by the above-mentioned amount, the solution of the energy equation where  $q$  is constant<sup>12</sup> gives the approximate critical dimension of the hot spot as 20 cm. The time for the temperature to increase by the above-mentioned amount is approximately 15 hours.

The minimum rate of air leakage where a fire can develop is, therefore,  $0.50 \text{ cc/cm}^2 \text{ min}$ . The minimum dimension of the pile is approximately 1.5 m.

From the calculations, the effect of diffusion is negligible when the rate of flow is  $1 \text{ cc/cm}^2\text{min}$ , and it seems likely that it can be assumed that it is still negligible for a flow of  $0.5 \text{ cc/cm}^2\text{min}$ . Therefore the effect of diffusion may not have to be considered in the spontaneous heating of wet coals, unless the drying time is much greater than that shown by the calculations.

However, it should be noted that the above calculations are very tentative. To obtain accurate results, not only more

exact methods of solving the energy equation should be used, but the processes, which become significant when the coal is in the stage before it is incinerated, should also be considered.

### 3. Applications to Spontaneous Heatings in Mines

It is noted that only heatings which result from the oxidation of coal are considered.

In storage piles, the coal is well compacted, and segregation of size is avoided, therefore air movement due to barometric pressure changes and to pressure differences due to wind, is small. The chimney effect is usually negligible. Therefore heatings, if occurring, are normally found on the windward side, and not very deep into the surface<sup>1</sup>.

Underground fire, however, is a much more common hazard, due to the physical conditions arising from mining practices. The fall of coal, the method of working where large piles of coal may be left for a long time, result in conditions where fires easily develop. Packing the coal piles cannot be done, therefore air leakage due to ventilation pressure gradients is aggravated. The poor thermal conductivity of rock and coal produces a favourable condition for the heating.

In New Zealand coal mines, it is usually found that about 60 to 80 percent of total mineable coal in a seam is lost through spontaneous heatings or suspected heatings. The fire is sometimes caused by fusain or sooty backs which is coal in a finely divided state. Pyrite occurs in disseminated form but has not been shown to play a part in the heatings.

The thickness of the seam and the bord and pillar method of working create the conditions which lead to fires. A certain

amount of coal is left on the roof, when this coal falls and the roof stone falls on the coal, a fire is most likely to occur. The fall of stone introduces energy to the heating which has not been considered. A mass of 5000 kgs of stone falling from 3 m height has a kinetic energy of the order 17 Kcal. If the fall strikes on an area of  $200 \text{ cm}^2$  it can raise the temperature of a layer of coal 10 cm deep approximately by  $44^\circ\text{C}$ . The time that signs of heating appear after a fall is usually found to be within weeks. The first indication of a heating is a sweetish smell, which is followed by wetting of the roof. Sealing off the area is the most common method to prevent the fire from spreading to other areas, but this usually means that the coal is lost. Cooling by increased ventilation is sometimes attempted, but previously there has been little experience or theory that the mine management can use as a guide.

This work may have some practical applications. Providing the correct data are used in the calculations, useful information can be obtained. The ventilation which would cause a pile to go on fire, the time when the fire appears, and its location in the pile can be found. The size of the fire can also be found. Safer ventilation may be deduced.

The air leakage into a pile of coal in a goaf is caused by the air movement and the underpressure due to ventilation. If the air velocity is taken as  $90 \text{ ft/min}^{48}$ , this air current when impinging to a pile of coal can cause a pressure head of  $0.5 \times 10^{-5} \text{ cm water}$ , which produces a flow of  $0.3 \text{ cc/cm}^2 \text{ min}$  over a pile 6 ft long of  $\frac{1}{10}$  coal. Wind velocity at intake

and return airways is much higher. A quantity of ventilation of 90,000 cfm causes a wind velocity 12 mph in a 20 ft diameter shaft, and this wind can cause an air leakage of  $25 \text{ cc/cm}^2 \text{ min}$  in a 6 ft length of  $\frac{1}{10}$ " coal. A pressure difference of 0.05 cm water caused by the ventilation can produce a flow of  $10 \text{ cc/cm}^2 \text{ min}$  through a thirty feet length of  $\frac{1}{10}$ " coal. The depth of the fires which have been observed<sup>88</sup> shows that there is considerable air leakage into a coal pile. The rate of air leakage into piles of coal can be measured and a correlation of the rate with the quantity of ventilation can therefore be obtained.

The specific heat of coals has been found to vary with moisture content<sup>32</sup>. However, it can be seen that the specific heat only affects the heating to a small extent, as the change in sensible heat in the initial stages is small compared with the heat of evaporation.

Stott<sup>96</sup> found that the percentage of slack coal in the coals as mined from various Southland mines, is about fifty percent. The size distribution of slack coals from different mines was found to be similar. About 65 percent are above  $\frac{1}{4}$ ", 26 percent are in the range of  $-\frac{1}{4}$ " + 10 mesh, 16 percent pass through 10 mesh. However, the percentage of fines and of dust in slack coals has been found to vary appreciably in individual samples<sup>96, 22</sup>. Deviations from a mean value are therefore high<sup>96</sup>. When lumps of coal are dropped from a height, the finer sizes are usually at the centre of the fall and surrounded by the coarser coal. A fall of stone on the pile may also increase the percentage of fines.

The amount of fires will increase a lot as the coal



is weathered, and therefore new faces are opened for the oxidation, because of the slacking property of sub-bituminous coals. It was found that for Waikato coal, the percentage of +1" coals was reduced from 77.6 percent to 4.7 percent in 31 days. The percentage of fines did not change as fast as that of coarse coals<sup>14</sup>. The degree of slacking is increased by alternately wetting and drying. After 34 days the process of wetting and drying increased the percentage of - $\frac{1}{8}$ " coal by 20 percent, while the increase in the unwetted coals was 3 percent<sup>76</sup>. However, in the above-mentioned experiments the coal was subjected to extreme conditions. In a pile of coal, the coal in the interior is protected by the external layers and the conditions would not be so severe, therefore the slacking would be less severe.

The moisture content of coal has been found to be fairly constant within each mine<sup>21,96</sup>. However, within one rank it varies considerably. Moisture content of sub-bituminous coals varies from 10 percent to about 25 percent. Moisture content of freshly mined lignites varies from 20 percent to more than fifty percent<sup>98</sup>. Although lignites are very reactive, they do not fire easily in underground mines. In storage piles, the moisture content of lignites changes as it comes into equilibrium with the ambient humidity. However, it is usually still over 20 percent<sup>60</sup> which gives some protection against heating.

Graham<sup>48</sup> found that temperatures in the majority of New Zealand mines reach a constant value after a distance of 1000 yards from the entry. Temperature in the mine can therefore be considered as constant, with little effect from

atmospheric temperature. During the winter, the temperature at different mines varies from 50°F to 60°F, in the summer the temperature varies from 60°F to 80°F. The air from the return was found to be always saturated. The average depth of most of New Zealand mines is approximately four to five hundred feet, therefore if an increase of 5.45°F is allowed for every 1000 ft of descent, the atmosphere of the working areas has a humidity of about 80 percent. This nearly saturated atmosphere increases the liability to heating in piles of coal in underground mines.

The above-mentioned factors should be investigated to provide accurate data on the conditions of piles of coal in underground mines, which would enable practical applications to be deduced from this work.

## CHAPTER EIGHT

### CONCLUSIONS AND FURTHER WORK

It was found that the change in temperatures of a column of coal, when being oxidised by a current of air, could be described within the limit of the experimental errors by a set of equations which describe the process of spontaneous heating.

The heating of the coal was computed from different values of the parameters in the rate of oxidation. Values of the activation energy of the order 39 Kcal/mole and an order of reaction from 0.4 to 0.5 were found to give temperature curves similar to those obtained in the experimental curves. The decrease in the rate of oxidation was found to be slower than that proportional to the power 0.9 of the extent of oxidation, but more rapid than that proportional to the power 0.27 of the extent of oxidation.

Using a vapour pressure - moisture content relationship, it was found that a pile of coal may go on fire if the air leakage is in the range  $1 \text{ cc/cm}^2 \text{ min}$  to  $20 \text{ cc/cm}^2 \text{ min}$ . This range probably extends to a wider range of flows.

The region where the fire takes place was found to be localised. Its dimension and distance from the surface was found to be proportional to the rate of flow.

For coals which have similar rates of oxidation and evaporation of moisture as those used in the computations, the approximate maximum length of a pile of coal which can be

considered as safe is 0.8 m x rate of flow (in cc/cm<sup>2</sup>min). For example, at a rate of air leakage of 5 cc/cm<sup>2</sup>min, piles of coal of length less than 4 m will not be heated to more than 70°C after 80 hours and the temperatures in the pile will fall quickly after this heating period. For the rates of air leakage greater than 0.5 cc/cm<sup>2</sup>min, diffusion was found to be negligible.

More accurate data are desirable. Therefore it is suggested that the following work should be continued.

Oxidation characteristics of coals of different sizes in the range - $\frac{1}{4}$ " should be obtained.

Drying characteristics of - $\frac{1}{4}$ " coal should also be measured for different temperatures and different rates of flow.

Low temperature oxidation tests should be used as a means of checking the applicability of the data obtained above to large-scale heatings.

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## APPENDIX 1

### HEAT OF OXIDATION EXPERIMENT

#### Microcalorimetry<sup>6,90</sup>

The equation expressing the rate of heat generated in the calorimeter as a function of the deflection of the galvanometer is

$$W = \frac{p}{g} \Delta + \frac{\mu}{g} \frac{d\Delta}{dt}$$

where  $W$  = rate of heat generation

$g$  = conversion factor from the temperature difference between the internal and external boundaries to the galvanometer deflection

$\Delta$  = galvanometer deflection

$p$  = heat transfer between the boundaries per second per degree temperature difference

$\mu$  = effective heat capacity of the calorimeter

$t$  = time

The effective heat capacity  $\mu$  is given by

$$\mu = C + D_p$$

where  $C$  = true heat capacity

$D_p$  = coefficient of thermal disequilibrium

The ratio  $\frac{p}{g}$  is usually measured by the Joule effect. The ratio  $\frac{\mu}{g}$  can be found from the transient deflection of the galvanometer.

When the apparatus is used for thermokinetic studies

of very slow processes, the term  $\frac{\mu}{g} \frac{d\Delta}{dt}$  is very small relative to  $\Delta$ , and the rate of heat generation is given by:

$$W = \frac{P}{g} \Delta$$

In the rising part of the recorded curve, the rate of heat generation can be obtained from:

$$\Delta = \Delta_0 (1 - e^{-wt})$$

where  $w = \frac{P}{\mu \Delta_0}$

$\Delta$  = transient deflection

$\Delta_0$  = deflection for the rate of heat generation at time  $t$ .

The sensibility of the apparatus depends on the nature of the thermocouples: thermoelectric power, thermal conductivity and electrical resistivity, and on the number, length and cross-sectional area of the couples.

The reproducibility of the apparatus is affected by:

- (i) Irregular distribution of the thermocouples.
- (ii) Parasitic thermoelectric e.m.f.'s.
- (iii) Thermal leakage by conduction in the top section of the cell and by convection by the flow of the gas through the calorimeter.

Therefore the heat conducted through the parts which lead from the calorimeter to outside should be kept as small as possible.

### Heat of Oxidation Experiment

The microcalorimeter used in the experiment had a sensitivity of  $2.7\mu\text{V}\cdot\text{cal/hr}$  and consisted of 84 couples of 28 gauge constantan and 36 gauge copper wires.

Estimated rate of heat generated by oxidation is 3 cc/100 gm hr for fresh  $\frac{1}{4}$ " coal. Therefore the heat generated in the calorimeter was  $0.6\text{ cal/hr} - 7\text{gm}$ .

Hypodermic tubes used for gas inlet and outlet to reduce the heat loss by conduction produced a pressure difference between atmosphere and inside the calorimeter equal to 29 mm Hg. Hence a rate of flow of 10 cc/min would cause a rate of cooling of  $0.625\text{ cal/hr}$ .

## APPENDIX 2

### CALCULATION PROCEDURE TO INCLUDE RADIAL HEAT CONDUCTION IN THE SIMULATION OF LABORATORY EXPERIMENTS

#### Radial Heat Conduction (Figure 1)

Finite difference formulae for radial heat conduction are formed as follows:

Let  $k = 1$  denotes the coal  
 $= 2$  denotes the glass  
 $= 3$  denotes the insulation  
 $j$  denotes radial increments

The increments in each material are equidistant.

Let  $a$  denote the term  $\alpha_k \left( \frac{\partial^2 T}{\partial r_k^2} + \frac{1}{r_k} \frac{\partial T}{\partial r_k} \right)$

where  $\alpha_k$  = thermal diffusivity

At the central section:

$$a = \frac{2\alpha_1}{\Delta r_2} \frac{\Delta T}{\Delta r_1}$$

at section  $j$  :

$$a = \alpha_k \left\{ - \frac{\Delta T_{j-1}}{(\Delta r_k)^2} + \left( \frac{1}{(\Delta r_k)^2} + \frac{1}{R_j} \right) \Delta T_j \right\}$$

where  $\Delta r_k$  = radial increment of material  $k$

$R_j$  = the inner radius of section  $j$

Heat balance at the glass section gives:

$$C_{p2} \rho_2 A \Delta r_2 (a) = 2\pi(R_j + \Delta r_2) K_3 \frac{\Delta T_j}{\Delta r_3/2} - 2\pi(R_j) K_1 \frac{\Delta T_{j-1}}{\Delta r_1/2}$$



where  $C_{p2}, \rho_2$  are the specific heat and density respectively of glass

$K$  = thermal conductivities

$A = 2\pi (R_j + \Delta r_2/2)$

$$\therefore a = \frac{1}{C_{p2} \rho_2} \left\{ \frac{K_3 (R_j + \Delta r_2)}{R_j \Delta r_2} \frac{\Delta T_j}{\Delta r_3/2} - \frac{K_1 R_j}{R_j \Delta r_2} \frac{\Delta T_{j-1}}{\Delta r_1/2} \right\}$$

The inner adjacent section:

$$a = \alpha_1 \left\{ \frac{R_j}{R_{j-1} \Delta r_1} \frac{\Delta T_{j-1}}{\Delta r_1/2} - \frac{R_{j-1}}{R_{j-1} \Delta r_1} \frac{\Delta T_{j-2}}{\Delta r_1} \right\}$$

The outer adjacent section:

$$a = \alpha_3 \left\{ \frac{R_{j+1} + \Delta r_3}{R_{j+1} \Delta r_3} \frac{\Delta T_{j+1}}{\Delta r_3} - \frac{R_{j+1}}{R_{j+1} \Delta r_3} \frac{\Delta T}{\Delta r_3/2} \right\}$$

Since the outermost section has a rectangular outer surface, the heat balance is:

$$V \times C_{p3} \rho_3 (a) = A_o K_3 \frac{\Delta T_j}{2 \Delta r_3} - A_i K_3 \frac{\Delta T_{j-1}}{\Delta r_3} + H A_o \frac{\Delta T_j}{2}$$

where  $V$  = volume/cm distance of the section

$A_o$  = Outer surface area

$A_i$  = inner surface area

$H$  = heat transfer coefficient

The interfacial temperature is taken as the average of the temperature of the section and the ambient temperature.

$$a = \frac{A_o}{V} \left\{ \alpha_3 \frac{\Delta T_j}{2 \Delta r_3} + \frac{H}{C_{p3} \rho_3} \frac{\Delta T_j}{2} \right\} - \frac{A_o \alpha_3}{V} \frac{\Delta T_{j-1}}{\Delta r_3}$$

### Convective Heat Transfer

Since the resistance to heat transfer is mainly by

conduction through the polystyrene, the convective heat transfer has negligible effect on the temperatures in the column. In the computations, the surface temperature is approximated as the average between the temperature of the first radial increment and that of the ambient. Dusingberre<sup>25</sup> proved that the approximation of the surface temperature is:

$$T_{(0,l)} = \frac{N}{1+N} T_a + \frac{1}{1+N} T_{(1,l)}$$

where  $T_{(i,l)}$  = temperature at radial increment  $i$ , time increment  $l$

$T_a$  = ambient temperature

$$N = \frac{h \Delta r}{k}$$

Elrod<sup>27</sup> gave an improved formula:

$$T_{(0,l)} = N F_1^* T_a + \{1 - (N+1) F_1^* T_{(0,l-1)}\} + F_1^* T_{(1,l)}$$

$$F_1^* = \frac{1}{N} \left( 1 - e^{-\frac{N^2}{M}} \operatorname{erfc} \sqrt{\frac{N}{M}} \right)$$

where  $M = \frac{(\Delta r)^2}{K \Delta t}$

When  $T_{(0,l)} \approx T_{(0,l-1)}$  the two formulae are the same.

For a temperature at the inner surface of the polystyrene of the order of 30°C, the surface temperature will be approximately 23.05°C for a convective heat transfer coefficient of 0.45 cal/cm<sup>2</sup> hr °C. For  $\Delta r = 1.75$  cm in the computations the temperature at the first increment will be 23.1°C, that obtained by the above-mentioned formulae will be 23.18°C,

therefore the difference is negligible. Furthermore, data on the heat transfer coefficient for such small temperature difference are scarce, therefore it is impossible that more accuracy is attained by using the more precise formulae.

APPENDIX 3PROGRAM FOR THE LOW TEMPERATURE OXIDATION EXPERIMENTS

The program is shown in Figure 50. Figure 46 shows the scheme to solve the energy and continuity equations.

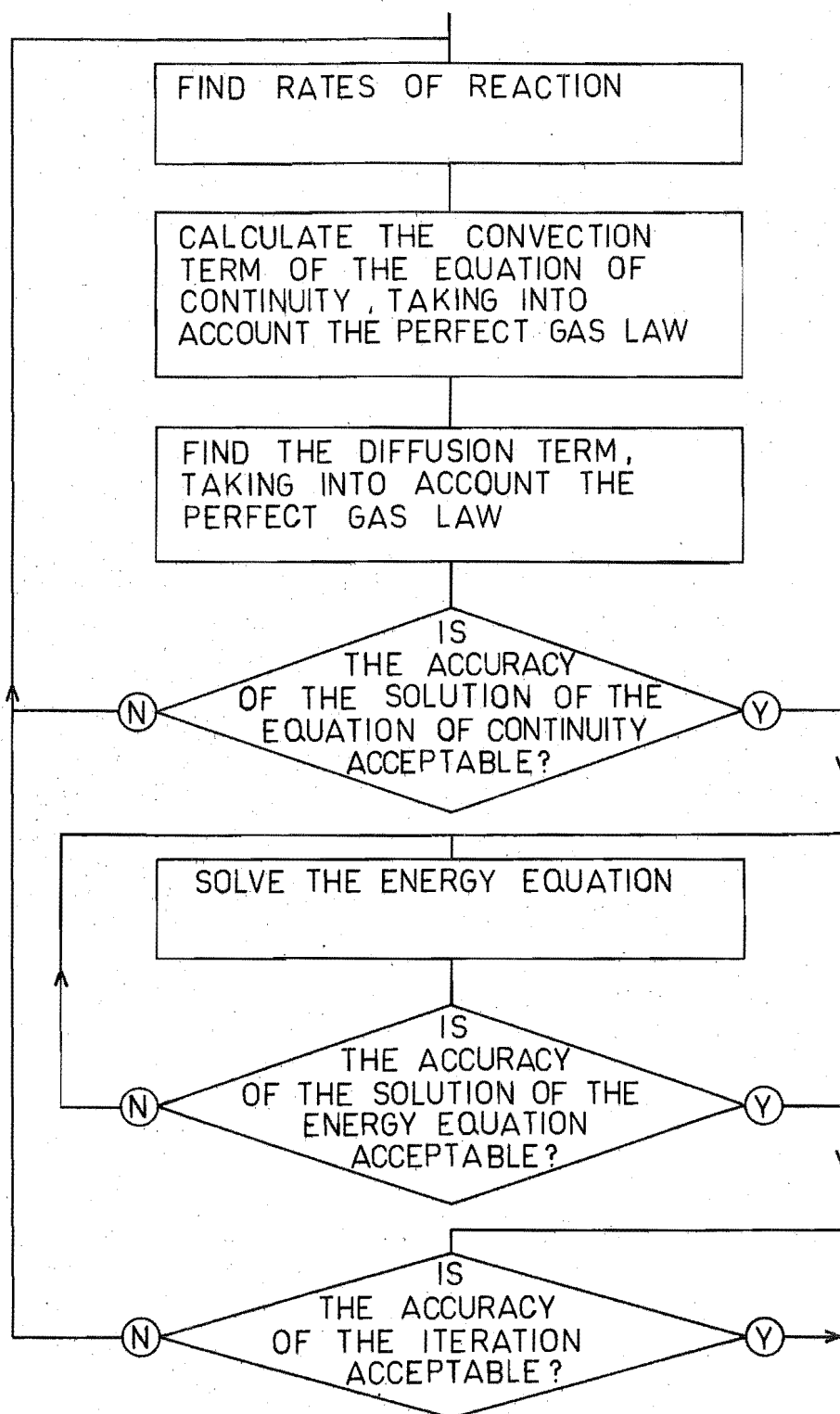
Phase PC

This phase reads the input variables and computes constant values.

Symbols

VEL	=	inlet velocity	$\text{cm}^3/\text{cm}^2\text{min}$
DETAX	=	increment in axial direction	cm
WC	=	initial moisture content of coal	gm/gm
WA	=	humidity of inlet air	gm/gm
N	=	number of increments in axial direction	
M	=	number of increments inside the glass tube in radial direction	
M1	=	total number of increments in radial direction	
DET2	=	time interval for output	hrs
DELTH	=	time increment	hrs
TAM	=	ambient temperature	$^{\circ}\text{K}$
POWER	=	power input to the heating system	watts
A1	=	temperatures, the values are read in as	$^{\circ}\text{C}$
SM	=	overrelaxation coefficients	
KODEDF	=	1 computation of diffusion is included	
		0 computation of diffusion is not included	
KODE IT	=	limit of number of steps for the iteration of the simultaneous equations of the solution of the energy equation.	

FIGURE 46. SOLUTION OF THE ENERGY AND CONTINUITY EQUATIONS



Phase PA

This phase prints output at time interval DET2.

Symbols

F1, F2, F3, F4, F5, F31, F8, F9, F81 = diffusivity and  
conductance terms

D1 = coefficients of the simultaneous equations from the  
approximation of the energy equation.

Subroutine PLOT

The output is printed in graphical forms.

Phase PB

The main part of the main program of this phase is to solve the simultaneous equations resulting from the finite difference approximations of the energy equation. The finite difference formulae are formed by using two time levels, as follows:

$$\begin{aligned}\frac{\partial T}{\partial t} &= \frac{1}{\Delta t} \{T_{(i, \ell+1)} - T_{(i, \ell)}\} \\ \left(\frac{\partial T}{\partial x}\right)_{i, \ell} &= \frac{1}{2\Delta x} \{T_{(i, \ell+1)} - T_{(i-1, \ell+1)} + T_{(i, \ell)} - T_{(i-1, \ell)}\} \\ \left(\frac{\partial^2 T}{\partial x^2}\right)_{i, \ell} &= \frac{1}{2(\Delta x)^2} \{T_{(i+1, \ell+1)} - 2T_{(i, \ell+1)} + T_{(i-1, \ell+1)} \\ &\quad + T_{(i+1, \ell)} - 2T_{(i, \ell)} + T_{(i-1, \ell)}\}\end{aligned}$$

The rate generation terms are:

$f(T, O_c, p_{O_2})$  = heat produced by oxidation

$g(T, Y(T))$  = heat due to moisture transfer.

$$\begin{aligned} \frac{dQ}{dt} = & \frac{1}{2} \left\{ (f(T, O_c, p_{O_2}))_{(i, l+1)} + f(T, O_c, p_{O_2})_{(i, l)} \right. \\ & - \frac{1}{\Delta x} \left( g(T, Y(T))_{(i, l+1)} (T_{(i, l+1)} - T_{(i-1, l+1)}) \right. \\ & \left. \left. + g(T, Y(T))_{(i, l)} (T_{(i, l)} - T_{(i-1, l)}) \right) \right\} \end{aligned}$$

where  $i$  denotes increment in the axial direction

$l$  denotes increment in time

The formulation of the finite difference formulae for radial conduction is as previously described. The resulting equations are solved by successive over-relaxation iterative method<sup>70</sup>.

The order of the equations is rearranged into a consistent order. The optimum overrelaxation coefficient is determined by trial, since it was not possible to evaluate the largest eigenvalue by methods such as the power iteration method. It was probably due to the nature of the eigenvalues of the system of equations from this type of problem, that the power method would not converge.

### Symbols

EP	=	outlet oxygen concentration obtained from the experiment
DB, DD	=	coefficients of the simultaneous equations
A1 $\equiv$ T	=	temperatures $^{\circ}\text{K}$
A6 $\equiv$ WH	=	heat of evaporation
AGI	=	total rate of flow at time $l$ ( $\text{cc}/\text{cm}^2 - \Delta \theta$ )
C7 $\equiv$ E	=	rate of flow of carbon dioxide ( $\text{cc}/\text{cm}^2 - \Delta \theta$ )
C5 $\equiv$ GI	=	total rate of flow at time $l+1$ ( $\text{cc}/\text{cm}^2 - \Delta \theta$ )

A4 = GJ = rate of flow without moisture at time  $l + 1$   
 $(\text{cc}/\text{cm}^2 - \Delta\theta)$

C5 = AGJ = rate of flow without moisture at time  $l$   
 $(\text{cc}/\text{cm}^2 - \Delta\theta)$

NGN = rate of flow of nitrogen at time  $l + 1$   $(\text{cc}/\text{cm}^2 - \Delta\theta)$

ANGN = rate of flow of nitrogen at time  $l$   $(\text{cc}/\text{cm}^2 - \Delta\theta)$

AE = rate of flow of carbon dioxide at time  $l$   $(\text{cc}/\text{cm}^2 - \Delta\theta)$

AVAP = rate of flow of water vapour at time  $l$   $(\text{cc}/\text{cm}^2 - \Delta\theta)$

VAP = rate of flow of water vapour at time  $l + 1$   $(\text{cc}/\text{cm}^2 - \Delta\theta)$

#### Subroutines RATE, SOLVE:

The coefficients of the system of equations for the approximation of the energy equation are computed.

#### Function OXID:

The rate of oxidation is calculated. If the temperature difference between the 2 time intervals is not small, the temperature - dependent term is computed by:

$$e^{-\frac{E}{RT}} = e^{-\frac{E}{RT_0}} e^{-\frac{E}{RT_0^2} (T - T_0)}$$

where  $T_0$  = temperature at time  $l$

$T$  = temperature at time  $l + 1$

#### Phase PE

The main program adjusts the oxygen absorption at each increment calculated by the rate equation, so that the total oxygen absorption in the column is that obtained experimentally.

The scheme is shown in Figure 47.



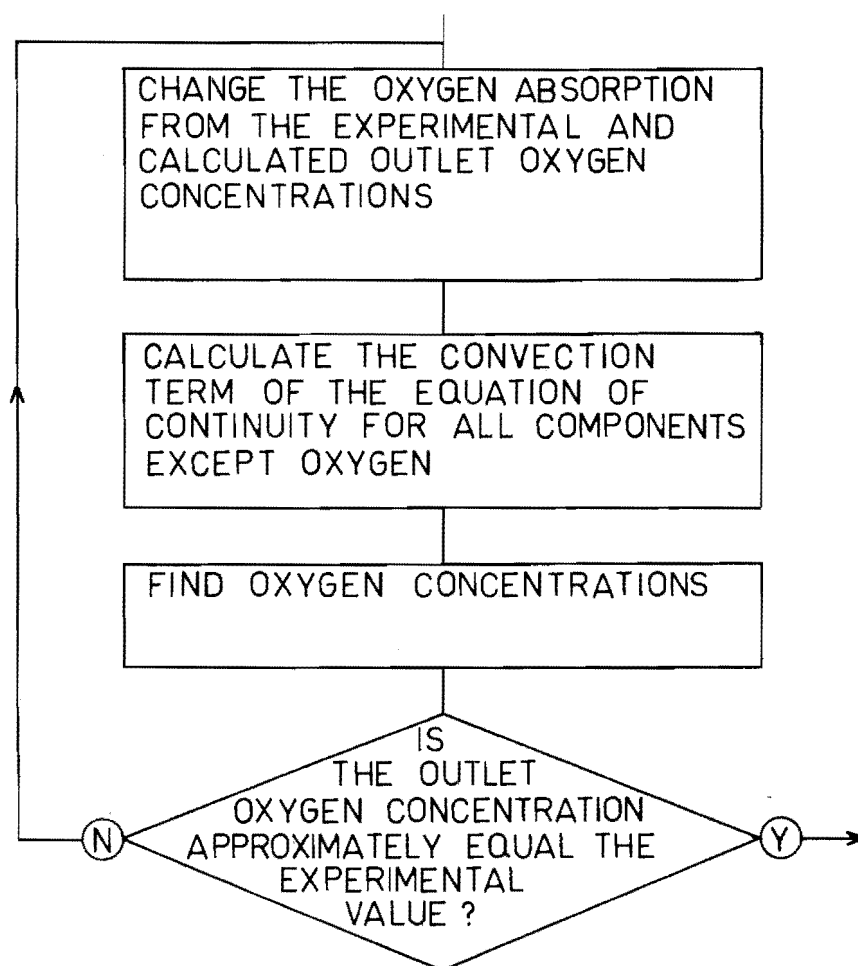


FIGURE 47 . CALCULATION OF THE RATES OF REACTION

Symbols

AK2 = ratios of the total oxygen absorption in the column  
measured experimentally over that calculated

AK = final mean value of AK2

Subroutine PSB

The diffusion term of the continuity equation is solved.

The simultaneous equations obtained from the finite difference approximations of the diffusion in cylindrical coordinates were so ill-conditioned that their iteration sometimes diverged.

Therefore the equation is written as

$$\frac{X_{k+1} - X_\ell}{\Delta \theta} = \frac{D}{2} \left\{ \left( \frac{\partial^2 X}{\partial x^2} + \frac{\partial^2 C}{\partial r^2} \right)_{k+1} + \left( \frac{1}{r} \frac{\partial X}{\partial r} \right)_k + \left( \frac{\partial^2 X}{\partial x^2} + \frac{\partial^2 X}{\partial r^2} + \frac{1}{r} \frac{\partial X}{\partial r} \right)_\ell \right\}$$

where  $X_k$  and  $X_{k+1}$  are intermediate values of  $X_{\ell+1}$ .

The value  $X_{k+1}$  is computed from the values of  $X_k$  and  $X_\ell$  by finite difference approximation. The resulting simultaneous equations are nearly symmetric, their iteration converges quickly.  $X_{k+1}$  are iterated to their final values  $X_{\ell+1}$ . The scheme is shown in Figure 48.

Symbols:

$$\text{HDETAX} = (\Delta x)^2$$

$$\text{HDELR1} = (\Delta r)^2$$

BA, BB, BD, BE, S = Coefficients of the simultaneous equations

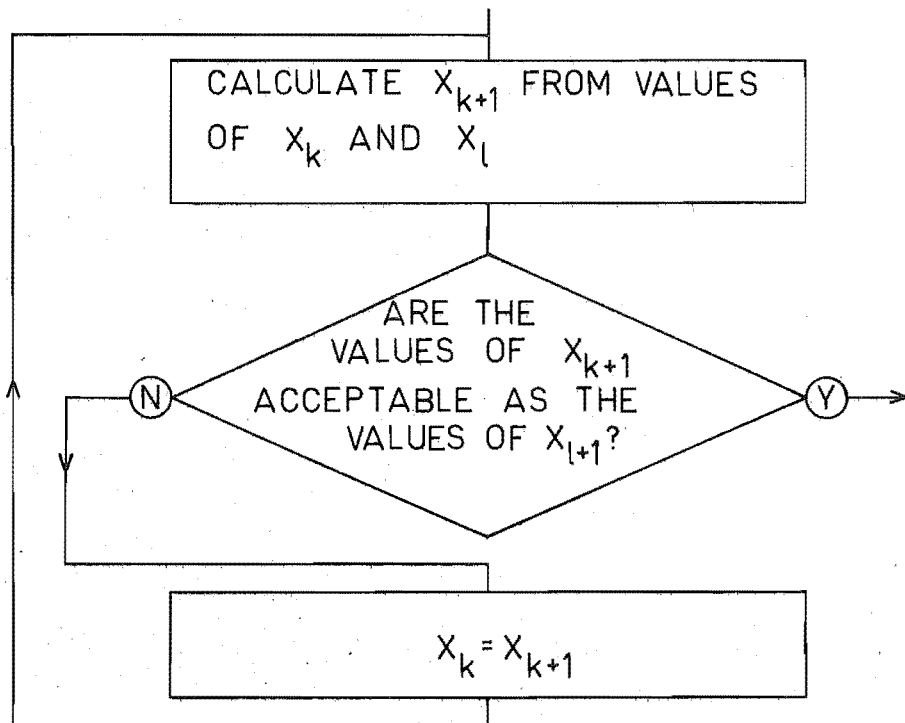


FIGURE 48. SOLUTION OF THE DIFFUSION EQUATION

BP = concentrations of component i at time  $t$   
 P = concentrations of components i at time  $t$  plus  
 the change due to diffusion.

#### Subroutine DSQRTA

New values of a variable which is being iterated are computed from values from 3 previous iteration steps, according to Aitken  $\delta^2$  formula.

#### Symbols:

P = values at step m  
 AAA = values at steps m - 1 and m - 2

#### Subroutines ZAA, ZAB

These subroutines support an abbreviated IBCOM// subroutine.

#### Performance of the program:

Results obtained for different values of  $\Delta r$ ,  $\Delta x$  and  $\Delta \theta$  showed that the accuracy was not affected by varying  $\Delta r$ ,  $\Delta x$  and  $\Delta \theta$ . Therefore the truncation errors by time increment and increments in the axial and radial directions are negligible.

The radial increment was varied from 0.5 cms to 1.5 cms for the coal, from 1.75 cm to 4.375 cms for the polystyrene. The axial increment was varied from 11.25 cms to 50 cms. Time increment was varied from 0.5 hrs to 6 hrs with no effect on the calculated results within  $0.1^\circ\text{C}$ . Using time increments of 3 hr, longitudinal distance increments of 50 cms and radial increments of 1.5 cm, the programmes can be completed in 20 min for 60 hrs of oxidation time if gas diffusion is neglected.

The inclusion of gas diffusion increases the calculation time to up to three hours. The long calculation times are caused by having to store parts of the programme in the disc memory of the IBM 360/44 computer used and it is likely that more efficient storage could reduce the computer time greatly.

# APPENDIX 4

## PROGRAM FOR THE ONE DIMENSIONAL CASE

The program is shown in Figure 51.

In this program, the vapour pressure - moisture content curves are used to compute the humidity of the air current. The humidity change term is therefore of the form:

$$g(\text{moisture content, temperature, humidity}) = g(W) k(T)$$

where  $W$  = moisture content of coal

$T$  = temperature

The energy equation is:

$$\begin{aligned} C_1 \rho_1 \frac{\partial T}{\partial t} &= K \frac{\partial^2 T}{\partial x^2} + C_2 \rho_2 V \frac{\partial T}{\partial x} \\ &- \Delta H_{H_2O} \left\{ \frac{\partial}{\partial x} (g(W) k(T)) \right. \\ &- \nabla j_{H_2O} + \frac{\partial}{\partial t} (\rho_{H_2O} w_{H_2O}) \left. \right\} \\ &+ \frac{dQ}{dt} \end{aligned}$$

The iterative procedure, in which the first and second derivations  $\frac{\partial T}{\partial x}$  and  $\frac{\partial^2 T}{\partial x^2}$  are approximated by finite difference formulae, only converges in a reasonable number of steps at low temperatures, where the conduction and convective terms are still appreciable in comparison with other terms. At high temperatures, the energy equation can be expressed mainly by:

$$\rho_1 C_1 \frac{\partial T}{\partial t} = \frac{dQ}{dt} - \Delta H_{H_2O} \cdot \left\{ k(T) \left( \frac{\partial Y}{\partial W} \right) \frac{\partial W}{\partial x} + g(W) \left( \frac{\partial Y}{\partial T} \right) \frac{\partial T}{\partial x} \right\}$$

$\frac{\partial Y}{\partial W}$  and  $\frac{\partial Y}{\partial T}$  are also functions of  $W$  and  $T$ .

### Phase PC

#### Symbols:

RATIOA = Value of the ratio of heat term due to moisture transfer over the heat term due to specific heat for a same temperature change.

LIMVAP = the vapour flow rate according to the value of RATIOA

#### Subroutine DCNP

Coefficients of the Tchebyshev series are evaluated.

### Phase PA

#### Subroutine PLOT

### Phase PB

#### Subroutine DIFFLN

The equation of continuity is solved.

#### Symbols

JJJJJJ = number of times the equation of continuity and the energy equation have been computed in one time step.

ENDA, ENDB = boundary values of the diffusion equation.

#### Subroutine PSB

The diffusion term of the continuity equation is solved.

#### Subroutine DSQRTA

#### Function OXID

Subroutine RATE

The energy equation is solved.

When the flow of water vapour at a point is less than LIMVAP, the temperature is computed as follows:

$$T = A + \frac{\Delta t}{C_1 \rho_1} \left\{ K \frac{\partial^2 T}{\partial x^2} + C_2 \rho_2 V \frac{\partial T}{\partial x} - \Delta H_{H_2O} \left( \frac{\partial}{\partial x} (g(W) k(T)) \right) - v_{j_{H_2O}} + \frac{\partial}{\partial t} (\rho_{H_2O} w_{H_2O}) \right\} + \frac{dQ}{dt}$$

When the flow of water vapour exceeds LIMVAP, the temperature is computed as follows:

$$\text{Let } a = \frac{dQ}{dt} + K \frac{\partial^2 T}{\partial x^2} + C_2 \rho_2 V \frac{\partial T}{\partial x} + \Delta H_{H_2O} \left\{ v_{j_{H_2O}} - \frac{\partial}{\partial t} (\rho_{H_2O} w_{H_2O}) + g(W_{(i-1)}) k(T_{(i-1)}) \right\}$$

where  $i-1$  denotes the previous point.

The equation  $C_1 \rho_1 \frac{\partial T}{\partial t} = \Delta H_{H_2O} \{g(W) k(T)\}$  is then solved iteratively as follows: The root of the equation

$$\Delta H_{H_2O} \{g(W) k(T_{av})\} + a - C_1 \rho_1 \left( \frac{T_k - T_l}{\Delta t} \right) = 0$$

is found, which gives the average vapour pressure and the corresponding  $T_{av}$ . Therefore the new approximation of the temperature at time  $l+1$  is given by the following equation:

$$g(W) k(T_{av}) - g(W) k(T_l) = g(W) k(T_{k+1}) - g(W) k(T_{av})$$



The corresponding  $T_{k+1}$  is found from the value of vapour pressure  $g(W) k(T_{k+1})$  obtained.  $T_k$  is replaced by  $T_{k+1}$  and the iteration is continued until  $T_{k+1}$  converges to a final value.

It can be seen that if LIM VAP is the value at which the heat change by specific heat is equal to the heat change due to humidity change, for the same temperature change, then at humidities above that corresponding to LIM VAP, the iteration always converges.

The values of the variable at successive iterative steps always oscillate about the final solution, therefore the extrapolation:

$$T_{k+1} = (T_k + T_{k-2}) / 4 + T_{k-1} / 2$$

can be used.

It is noted here that in this program  $T_{k+1}$  is found from the corresponding vapour pressure by finding the root  $T$  of the equation:

$$g(W) k(T) - \text{vapour pressure} = 0$$

If a reasonably accurate expression for  $T = f(\text{vapour pressure, moisture content})$  can be found, the procedure of solving the energy equation is simple. The scheme is shown on Figure 49.

### Symbols

ERS = error limit

### Subroutine VAPPRE

Vapour pressure =  $g(W) k(T)$  is computed. The temperature - vapour pressure of a free surface and moisture content - vapour

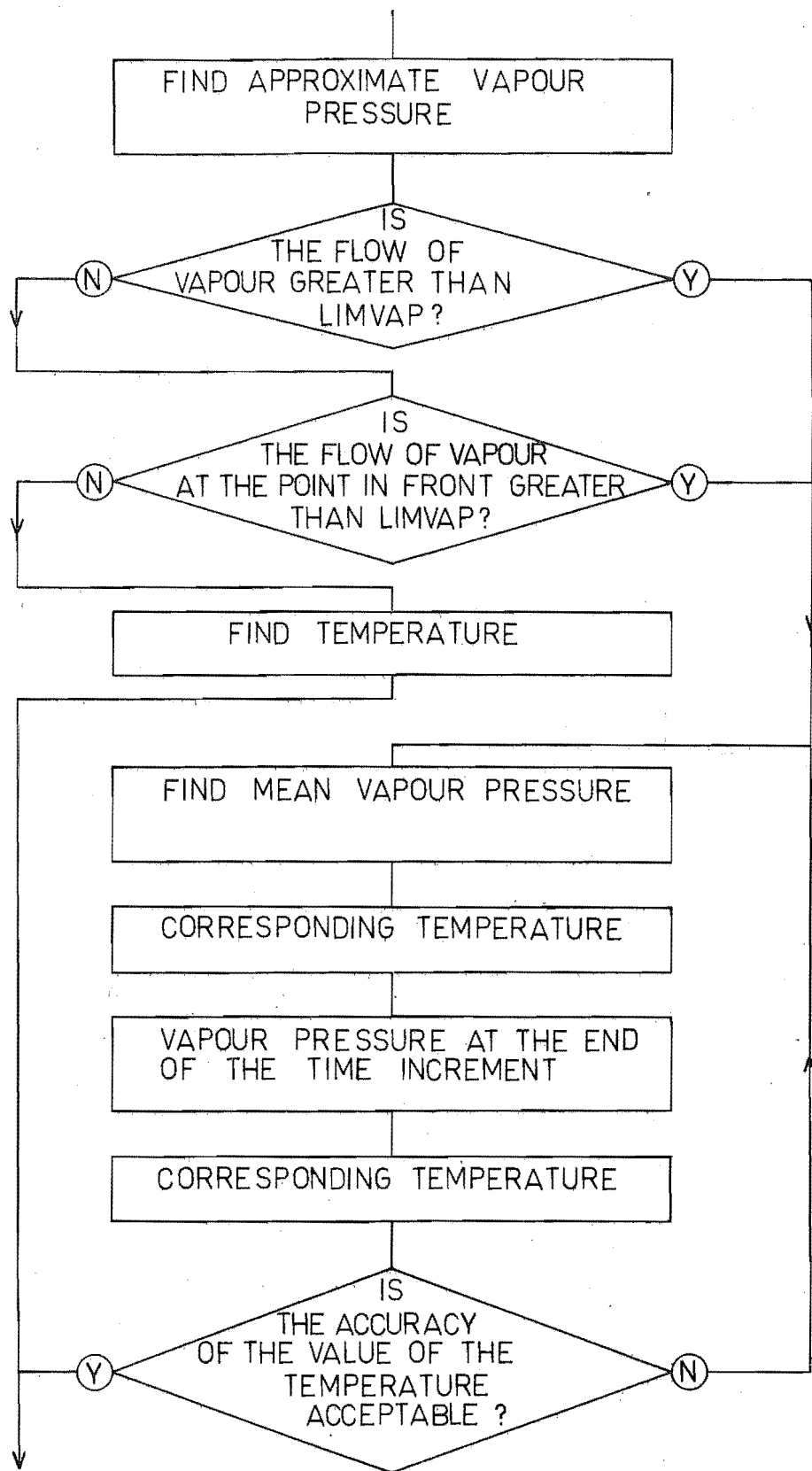


FIGURE 49. SOLUTION OF THE ENERGY EQUATION

pressure at 20°C are fitted with rational Tchebyshev series. Moisture content - vapour pressure at other temperatures are found by the Clapeyron-Clausius equation.

### Symbols

VAPPRE = humidity gm/gm

### Function FTCA

$$g(W) \quad k(T_{av}) - \frac{C_1 p_1}{\Delta H_{H_2O}} \left( \frac{T_k - T_\ell}{\Delta t} - \frac{a}{\Delta H_{H_2O}} \right) = 0$$

where  $T_{av}$  is the unknown variable, is set up.

### Function FTCB

$$g(W) \quad k(T_{k+1}) - g(W) \quad k(T_{av}) + g(W) \quad k(T_\ell) - g(W) \quad k(T_{av}) = 0$$

where  $T_{k+1}$  is the unknown variable, is set up.

### Subroutine DRTMI

The root of the above-mentioned equations is found by Muller's iteration method.

### Subroutine SIDQ

The resulting simultaneous equations in one dimension are solved by a direct elimination method.

### Symbols:

AAI, BBI, CCI, DDI = Coefficients of the equations

ERROR = limit of error

RATIO = scaling factor

R = residuals

RMAX = maximum residual.

APPENDIX 5DRYING RATE

The moisture is evaporated by the heat generated from the oxidation. Temperature gradient in the solid due to evaporation of moisture is negligible. Consider a large particle,  $d = 0.625$  cm, whose rate of drying is  $0.05$  gm/gm hr. Assume that the drying takes place within the region bounded by  $d_0 = \frac{1}{4} d$ . The heat required is  $24.6$  cal/hr  $\text{cm}^3$ . If this amount of heat is transferred from the surface where the oxidation takes place, a temperature gradient of  $0.067^\circ\text{C}$  from the surface to the drying region exists.

At the range of rates of flow which are under consideration, the resistance to vapour transfer in the gas phase is negligible. Consider an air path of cylinders, having the same diameter as the particles. Assume that the humidity at the interface is at equilibrium with the moisture content of the solid, and the mass flow of vapour from the surface of the particles into the gas does not affect appreciably the mass transfer coefficient.

The equation:

$$v(x) \frac{\partial H}{\partial y} = D \left( \frac{\partial^2 H}{\partial x^2} + \frac{1}{x} \frac{\partial^2 H}{\partial x} + \frac{\partial^2 H}{\partial y^2} \right)$$

with initial conditions:  $H(0, x) = f(x)$

= humidity of the air

entering the section

Boundary conditions :  $H(y, -\frac{d}{2}) = H_w = \text{equilibrium humidity}$

.  $H(y, +\frac{d}{2}) = H_w = \text{equilibrium humidity}$

describes the transfer of vapour in the gas phase. If  $v(x)$  is approximated by a mean value  $v$ , and transfer in the axial direction is negligible, the solution<sup>12</sup> for  $d = 0.625$  cm,  $D = 0.22$  cm<sup>2</sup>/sec,  $v = 0.16$  cm/sec shows that the concentration of vapour at the centre of the path can reach 98 percent of that at the wall when the air has travelled through a distance of 0.06 cm. At higher rates of flow, eddy mixing becomes significant. Therefore the humidity of the gas can be considered as uniform.

In the solid, the transfer of moisture to the surface by capillarity is faster than by molecular processes.

No data are available on the sorption equilibrium curves for New Zealand sub-bituminous coal, therefore a relationship was assumed, based on the results obtained by Kreulen<sup>64</sup>. The curves are shown on Figure 26. Equilibrium probably can be reached only at very low rates of flow.

Drying rate curves, shown on Figure 27, have recently been obtained at the Chemical Engineering Department, University of Canterbury. For scaling up, more data are required. However, it can be seen that the gas nearly reached saturation humidity, therefore it is likely that equilibrium is attained in the large scale process at the rates of flow used in these experiments. The curves give a rough indication of the shape of the equilibrium curves.

## APPENDIX 6

### TEMPERATURE AND TIME OF DRYING

The assumption that the air current reaches full saturation humidity introduces an excessive cooling effect, which when the rate of oxidation has been reduced by the extent of oxidation, cannot be kept up by the heat generated at any temperature, because the rate of heat production will only evaporate moisture at a rate at which the air current cannot attain full saturation. Therefore the coal is cooled down if full saturation is assumed, whilst fractional saturation will allow the coal to be dried at a high temperature. By being able to maintain a high temperature, not only the rate of oxidation is increased, but the total oxygen absorption capacity is also increased. Therefore, the oxidation can provide much more heat for the evaporation of moisture, and still maintain a rate which is capable of raising the temperature of the coal after the coal is completely dried.

The drying rate can be faster than in the case when full saturation is assumed, because the absolute humidity of a partially saturated air current at a high temperature can be higher than that of a fully saturated air current at a low temperature.

In the following example, it can be seen that if the relative vapour pressure, which is attained in the drying, is of the order 40 percent, the drying temperature can stay in the range 70°C to 90°C. The calculations of the transfer processes are simplified.

Assume that when the flow is  $1 \text{ cc/cm}^2 \text{ sec}$ , the first 1 m length of the pile requires an absorption of 30 cc/ml volume to dry out 0.1 gm/ml volume of moisture.

Assume that at this moisture content, 0.04 gm/ml volume, the temperature is still in the range  $50^\circ\text{C}$  to  $90^\circ\text{C}$ . If the temperature of the surface is at  $20^\circ\text{C}$ , the following heat balance is obtained:

Temperature $^\circ\text{C}$	Rate cc/100gm-hr	Heat Produced per 100 ml cal/hr	Heat Lost Con- duction cal/hr	Con- vection cal/hr	Remaining Heat cal/hr
50	0.72	1.51	.72	.56	0.23
60	1.6	3.36	.96	.74	1.66
70	3.4	7.14	1.2	.93	5.0
80	6.9	14.5	1.44	1.12	11.9
90	13.5	28.0	1.68	1.30	25.0

At the rate of flow of  $1 \text{ cc/cm}^2 \text{ hr}$ , the remaining heat can evaporate moisture at a rate which produces a relative humidity as follows:

Temperature $^\circ\text{C}$	Absolute Humidity gm/gm	Relative Humidity percent
50	0.005	6
60	0.0363	24
70	0.109	39
80	0.26	47
90	0.547	38

Therefore, if the moisture is evaporated at a rate where the air current can reach a humidity of 40 percent, the coal can be dried at a temperature ranged between  $70^\circ\text{C}$  to  $90^\circ\text{C}$ .

The heat balance after all the moisture has been evaporated is as follows:

Temperature	Drying Time	Total Oxygen absorbed	Rate of oxidation	Remaining heat after heat losses have been accounted for
°C	hr	cc/ml volume	cc/100gm hr	Cal/hr
50	10345	82.0	0.3	-
60	1445	46.1	1.1	0.61
70	480	41.4	2.57	3.14
80	201	39.7	5.42	8.82
90	96	39.0	10.75	19.59

The figures show that the drying temperature and drying time depends on the moisture content - vapour pressure relationship, and therefore the possibility of the coal to go on fire also depends on this relationship. The determination of accurate drying data for coal is thus of extreme importance in this problem.